NASA CR-54280
REPORT SM-46221-Q2

INORGANIC ION EXCHANGE MEMBRANE FUEL CELL

PERIOD ENDING 10 JANUARY 1965

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3-6000

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QUARTERLY PROGRESS REPORT SM-46221-Q2

INORGANIC ION EXCHANGE MEMBRANE FUEL CELL

by

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prepared for

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January 1965

CONTRACT NAS 3-6000

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1.0 SUMMATION AND CONCLUSIONS

The development and evaluation of zirconium phosphate ion exchange membranes for hydrogen-oxygen fuel cell application were continued. Target fuel cell performance characteristics for this program are the attainment of current density levels of 25-50 ma/cm^2 at a minimum of 0.5 volts during continuous fuel cell operation for at least 300 hours.

The results, discussions and conclusions reported here are based on the work performed during the second quarter of this program. This effort included fuel cell studies and membrane composition, fabrication and evaluation studies. A program for the next quarter is presented.

1.1 Fuel Cell Studies

Twenty-two fuel cell determinations were performed as five fuel cells were placed in operation. This effort was concentrated on one type of zirconium dioxide - phosphoric and "Zeolon H" membrane having a transverse strength of about 5,000 psi. Up to the first half of the current report period, fuel cell life tests were conducted at a voltage level of 0.5; thereafter, based on the recommendations of the NASA-Lewis project monitors, fuel cell tests were conducted at a constant current level of 30 ma/cm^2.

It is evident from these tests that this type of membrane is capable of performing for at least 1,000 hours and at temperatures of at least as high as 75°C at significant output levels. In a test conducted at 67°C, a 20 percent improvement in performance was effected during a 300-hour life test by the incorporation of platinum catalyst into the outer one-third layer of the membrane structure by a special sintering technique. In this instance, cell resistance was one-fourth to one-third the level usually recorded during this investigation. Moreover, the most stable performance to date has been recorded for a fuel cell involving a membrane whose free or unincorporated H_3PO_4 was leached prior to assembly.

Studies in the 75° - 90°C range indicate that the membranes can perform at the desired output level by proper fuel cell water management.

1.2 Membrane Composition, Fabrication and Evaluation Studies

Essentially, this phase of the program was completed during this quarter. The objective was to determine the effect of various zirconium dioxide-phosphoric acid mixture ratios as well as processing sintering temperatures on certain properties of the composite zirconium dioxide-phosphoric acid - "Zeolon H" membrane. The concentration of zirconia in the presintered mixture was varied from 30 to 85%. Such properties as transverse strength, resistivity and hydrolytic stability were studied. Significant results are outlined below.

Transverse strength: Maxima were obtained when the concentration of zirconia in the presintered mixture was at 50% and in the 80-85% range, depending on the presintering temperature. Both maxima were at similar levels of 5,000 - 5,500 psi. It was found possible to increase the transverse strength to as high as 9520 psi by saturating the sintered membrane with phosphoric acid through three impregnations, each being followed by sintering at 500°C for five minutes.

1.3 Membrane Resistivity

Measurements were performed at 70°, 90° and 105°C at relative humidity ranging from 26 to 83%. Generally, resistivity values are independent of membrane composition when sintering temperature is equal to or less than 500°C. At sintering temperatures of 800°C, however, resistivities increase with increasing zirconia concentration. Presintering temperatures of the initial zirconia-phosphoric acid mixture have little or no effect on resistivity. Sintering temperature of the final mixture involving "Zeolon H" has a significant effect on resistivity. Resistivities increase with sintering temperature to the largest extent when the sintering temperature increases from 500°C to 800°C.

The membrane system comprised of zirconia and phosphoric acid in a 50/50 weight ratio in the presintered mixture was analyzed most extensively. Relationships between membrane resistivity and relative humidity and Arrhenius plots relating resistivity with temperature indicate strong tendencies for membrane resistivities to decrease with increasing temperature, especially at higher relative humidities.

1.4 Hydrolysis Studies

Membranes were analyzed for percent of phosphoric acid liberated after immersion in water heated at 73° - 75°C for two hours. In addition a number of membranes were analyzed for phosphate content after being used in a fuel cell run.

Membrane composition and presintering temperatures have relatively little effect on the extent of phosphoric acid liberated. However, sintering temperature does exert a controlling influence, except when the ratio of phosphoric acid to zirconia in the presintered mixture is above one.

As for membranes evaluated at the end of fuel cell runs, it was found that a small loss in unreacted phosphoric can occur gradually during fuel cell operation. The loss in phosphate content appears to be that of free unicorporated phosphoric acid which apparently does not serve a critical function. This is borne out by an experiment currently in progress wherein a membrane which had lost 5.5% of its weight in phosphoric acid by prior soaking in water at 75°C is maintaining excellent performance in a fuel cell run for over 168 hours.

2.0 INTRODUCTION

The results of the previous program carried out under NASA Contract NAS 7-150 demonstrated that the inorganic ion exchange membrane comprised of the zirconia-phosphoric acid - "Zeolon H" combination could be prepared by ceramic technology at transverse strength levels of over 5,000 psi[1]. Adequately high conductivities and promising fuel cell performance had been obtained for these membranes at that time.

The program during the last quarter was concerned mainly with membrane improvement through a planned composition and fabrication study. It was established early that only membranes having transverse strengths of at least 5,000 psi manifested noteworthy fuel cell properties. One such membrane was selected for extensive fuel cell life tests that remain in progress to date.

During this quarter, the planned membrane composition and fabrication study was completed together with accompanying transverse strength, resistivity and hydrolytic stability measurements. In addition, a procedure for achieving a transverse strength of as high as 9520 psi was established.

As it had been shown that a membrane having a transverse strength of 5,000 psi could essentially fulfill the power requirements over a 300-hour fuel cell run in the 60^{o}- $75^{o}C$ temperature range, emphasis has been shifted to effecting improvement in fuel cell design as well as in the electrode-catalyst configuration to realize the optimum capabilities of these membranes.

In this report are the significant results obtained during the second quarter on fuel cell life tests extended to temperatures as high as $90^{o}C$. The principal results from the membrane composition and fabrication study are given together with accompanying interpretations based on physical property evaluations. Finally, the direction of the effort for the third quarter is outlined.

3.0 EXPERIMENTAL PROCEDURE, RESULTS AND DISCUSSIONS

3.1 Fuel Cell Life Tests

During the current report period, 22 tests were performed, as a total of five test cell units were placed into operation. Four of the cells were built according to the description given in the previous Quarterly Report[2], Figure 1, and the fifth cell was from a previous program. Up to about the midpoint of this report period, fuel cell tests were performed at a constant 0.5 volt. Then, following the meeting of November 19 and 20, 1964, with NASA-Lewis personnel, it was decided to operate thereafter at a constant current level.

Most tests were performed in the 60°-70°C range. One test was run at ambient temperature. Since highly satisfactory results were obtained with the membrane of principal interest, the C200B membrane, tests were extended to the 90°C level. The results obtained for 14 tests depicting the most significant results are given in Table I where current densities at 0.5 volt are listed. Tests 2, 6, 7, 9, and 12 had been run at constant current and their current outputs corresponding to 0.5 volts as obtained from polarization data are given. In Table II, pertinent data obtained for these constant current tests, as well as those for Tests 13 and 14, are listed separately.

Referring to Table I, except for Test 3, all tests were performed with the same basic membrane C200B. This membrane had been prepared from a 1:1 mixture of zirconium dioxide and phosphoric acid which had been sintered at 200°C; this is referred to as the presintering stage in the following discussions. After being ground to a fine state, the sintered mixture was mixed with equal parts by weight of phosphoric acid and "Zeolon H" and the final mixture was sintered at 500°C. The C400A membrane of Test 3 was prepared in the same manner except that the presintering temperature was 400°C and the sintering temperature was 300°C. As listed in the previous Quarterly Report[2], the transverse strengths of the C200B and C400A membranes were 5157 psi and 5370 psi, respectively. Actually, Test 3 is a continuation of Test 5 of Table III in that report.

The purpose of Test 1, conducted at ambient temperature, was to obtain a basis for comparison with fuel test data at ambient temperature

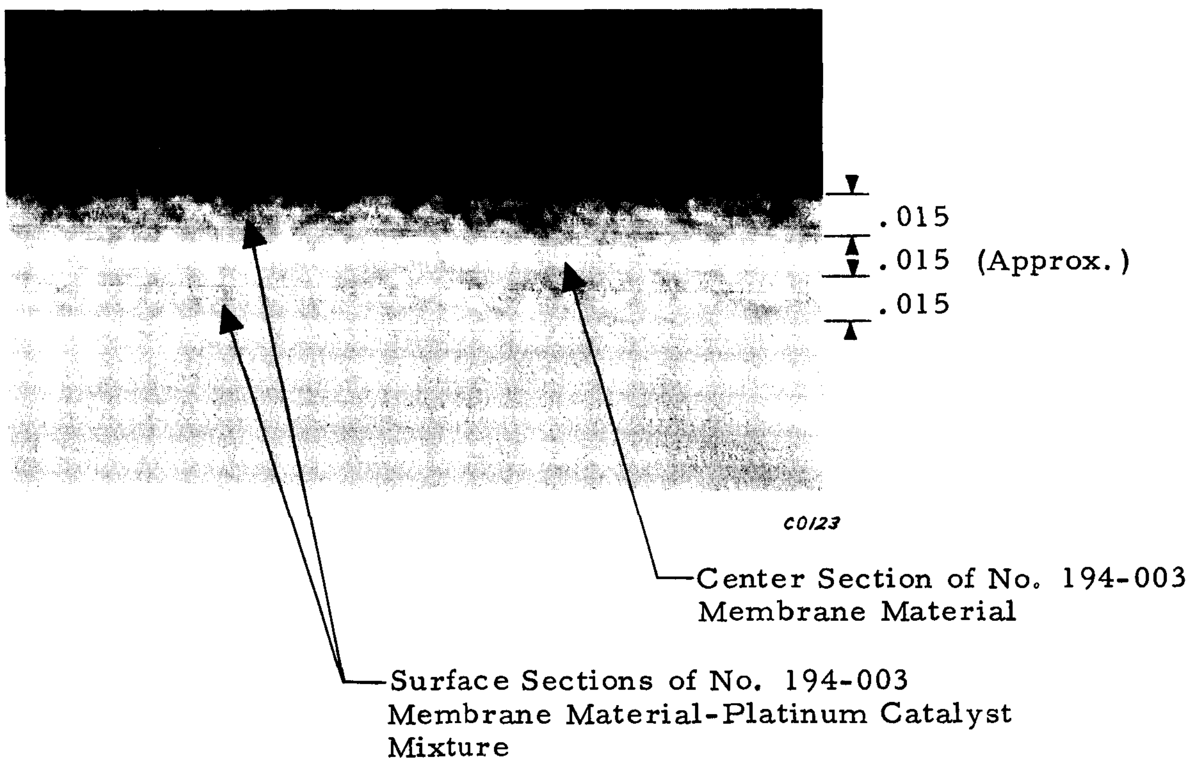

Figure 1. Fuel Cell Membrane - Catalyst Composite

TABLE I

INORGANIC MEMBRANE FUEL CELL OPERATING DATA ON PRE-SINTERED ZIRCONIUM DIOXIDE-PHOSPHORIC ACID-"ZEOLON H" MEMBRANE[a]

Fuel Cell Test No.	Membrane Identification Number	Membrane Thickness mm	Temperature, °C	Current Density, ma/cm^2 at 0.5v	Fuel Cell Resistance, ohms	Open Circuit Voltages, volts	Time of Measurement From Start of Run Hrs	Time of Run,[c] Hrs
1	C 200B	0.75(030")	25 ±1	20.0	1.97	0.860	92	624
				19.6	1.70	0.898	238	
				28.4	1.85	0.870	574	
2[b]	C 200B followed by three impregnation with phosphoric acid then impregnated with platinum	0.84(034")	60 ±1	26.9	1.55	0.933	97	Still operational after 291 hours
				26.9	1.55	0.965	115	
				31.0	1.43	0.952	195	
				33.0	1.31	0.952	199	
				35.0	1.27	0.965	291	
3	C 400 A	0.50(020")	61 ±1	36.2	1.33	0.950	5	584
				37.6	1.28	0.950	11	
				20.4	2.18	0.950	149	
				17.6	---	---	320	
				20.6	---	---	408	
				21.1	---	---	509	
4	C 200B	0.55	64 ±1	35.5	1.35	0.983	21	288[d]
				25.2	2.05	0.970	167	
				29.6	1.59	0.925	174	
				30.9	1.05	0.960	199	
				27.5	---	0.958	271	

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TABLE I (CONT'D)

INORGANIC MEMBRANE FUEL CELL OPERATING DATA ON PRE-SINTERED ZIRCONIUM DIOXIDE-PHOSPHORIC ACID-"ZEOLON H" MEMBRANE[a]

Fuel Cell Test No.	Membrane Identification Number	Membrane Thickness, mm	Temperature, °C	Current Density, ma/cm^2 at 0.5v	Fuel Cell Resistance, ohms	Open Circuit Voltages, volts	Time of Measurement From Start of Run, Hrs	Time of Run,[c] Hrs
5	C 200B	0.67	64 ±1	51.5	0.62	0.908	4	1,174
				51.8	0.53	0.790	29	
				43.8	0.55	0.755	54	
				43.8	1.25	0.790	78	
				39.6	1.66	0.765	215	
				38.3	1.03	0.793	239	
				33.5	1.05	0.805	315	
				33.1	1.03	0.812	357	
				32.2	1.10	0.815	360	
				26.9	1.23	0.805	502	
				27.0	1.39	0.862	652	
				22.2	1.62	0.860	675	
				23.2	1.56	0.848	679	
				22.8	1.55	0.859	947	
				20.5	1.85	0.882	919	
				18.2	1.90	0.863	1,016	
				20.4	1.88	0.880	1,057	
6[b]	C 200B followed by three impregnations with phosphoric acid	0.85	64 ±1	33.2	1.30	0.980	23	219
				36.1	1.18	0.972	101	
				36.0	1.23	0.977	124	
7[b]	C 200B followed by three impregnations with phosphoric acid	0.85	66 ±1	54.6	0.69	0.957	11	171
				50.3	0.78	0.950	67	
				49.2	0.83	0.950	91	
				24.3	1.78	0.945	164	

(cont. next page)

TABLE I (CONT'D)

INORGANIC MEMBRANE FUEL CELL OPERATING DATA ON PRE-SINTERED ZIRCONIUM DIOXIDE-PHOSPHORIC ACID-"ZEOLON-H" MEMBRANE[a]

Fuel Cell Test No.	Membrane Identification Number	Membrane Thick-ness, mm	Tempera-ture, °C	Current Density, ma/cm^2 at 0.5v	Fuel Cell Resist-ance, ohms	Open Cir-cuit Volt-ages, volts	Time of Measure-ment From Start of Run, Hrs	Time of Run,[c] Hrs
8	C 200B	0.52	67 ±1	59.0	0.77	0.970	95	241[d]
				56.8	0.83	0.970	100	
				58.0	0.82	0.970	116	
				53.2	0.90	0.962	121	
				34.4	0.71	0.940	193	
9[b]	C 200B Same as for Test 6 and 7, then impregnated with platinum	0.84	67 ±1	62.5	0.25	0.920	8	319
				57.5	0.27	0.928	32	
				51.3	0.26	0.920	55	
				42.5	0.36	0.810	152	
				37.5	0.38	0.805	175	
				35.8	0.36	0.760	195	
				34.0	0.41	0.825	223	
				40.0	0.39	0.900	248	
				39.0	0.38	0.915	313	
10	C 200B	0.56	75 ±1	18.8	2.15	0.875	21	52
				21.5	1.85	0.852	27	
				19.3	2.30	0.872	44	
				20.0	---	---	51	
11	C 200B	0.53	75 ±1	31.5	1.70	0.970	3	912[d]
				23.7	2.23	0.932	23	
				23.0	2.31	0.932	52	
				26.3	1.87	0.955	76	
				22.8	2.29	0.970	191	

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TABLE I (CONT'D)

INORGANIC MEMBRANE FUEL CELL OPERATING DATA ON PRE-SINTERED ZIRCONIUM DIOXIDE-PHOSPHORIC ACID-"ZEOLON-H" MEMBRANE[(a)]

Fuel Cell Test No.	Membrane Identification Number	Membrane Thick-ness, mm	Tempera-ture, °C	Current Density, ma/cm^2 at 0.5v	Fuel Cell Resist-ance, ohms	Open Cir-cuit Volt-ages, volts	Time of Measure-ment From Start of Run, Hrs	Time of Run,[(c)] Hrs
11	C 200B	0.53	75 ±1	30.6	1.55	0.972	340	
				28.5	1.72	0.965	363	
				23.4	2.11	0.952	388	
				26.1	1.80	0.942	532	
				22.2	2.28	0.955	604	
				21.8	2.21	0.980	701	
				19.4	2.54	0.972	774	
				21.5	2.29	0.962	841	
12	C 200B	0.74	80 ±1	23.2	1.21	0.730	120	149
				30.5	0.89	0.740	144	
13	Results given in Table II only, as no polarization data were taken.							
14	Results given in Table II only, as no polarization data were taken.							

(a) Except for Test 3, all tests were performed with C 200B membrane.
(b) Test run at constant current density of 30 ma/cm^2.
(c) Unless otherwise noted, test did not fail but was terminated either for diminished performance or else, met 300-hour life requirement.
(d) Test failed.

TABLE II

INORGANIC MEMBRANE FUEL CELL OPERATING DATA ON PRE-SINTERED ZIRCONIUM DIOXIDE-PHOSPHORIC ACID- "ZEOLON H" MEMBRANES

Tests Conducted at Constant Current Density of 30 ma/cm^2

Fuel Cell Test No.	Membrane Identification Number	Membrane Thick-ness, mm	Tempera-ture, °C	Cell Volt-age, volts	Fuel Cell Resist-ance, ohms	Open Cir-cuit Volt-ages, volts	Time of Measure-ment From Start of Run, Hrs	Time of Run,[a] Hrs
2	C 200B	0.84	60 ± 1	0.460	1.550	0.933	97	Test still in Progress
				0.460	1.550	0.965	115	
				0.510	1.432	0.952	195	
				0.533	1.313	0.952	199	
				0.532	1.210	0.965	291	
6	C 200B	0.85	64 ± 1	0.532	1.300	0.980	23	219[a]
				0.560	1.182	0.972	101	
				0.558	1.232	0.977	124	
7	C 200B	0.85	66 ± 1	0.639	0.687	0.957	19	171[a]
				0.620	0.780	0.950	67	
				0.618	0.825	0.950	91	
				0.414	1.791	0.945	164	
9	C 200B	0.84	67 ± 1	0.660	0.245	0.920	8	319
				0.650	0.271	0.928	32	
				0.635	0.256	0.920	55	
				0.590	0.364	0.810	152	
				0.557	0.377	0.805	175	
				0.543	0.358	0.760	195	
				0.528	0.410	0.825	223	
				0.574	0.385	0.900	248	
				0.571	0.378	0.915	313	
12	C 200B	0.74	80 ± 1	0.432	1.210	0.730	120	149[a]
				0.502	0.889	0.740	144	

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TABLE II (CONT'D)

INORGANIC MEMBRANE FUEL CELL OPERATING DATA ON PRE-SINTERED ZIRCONIUM DIOXIDE-PHOSPHORIC ACID - "ZEOLON H" MEMBRANES

Tests Conducted at Constant Current Density of 30 ma/cm^2

Fuel Cell Test No.	Membrane Identification Number	Membrane Thick-ness, mm	Tempera-ture °C	Cell Volt-age, volts	Fuel Cell Resist-ance, ohms	Open Cir-cuit Volt-ages, volts	Time of Measure-ment From Start of Run, hrs	Time of Run,[a] Hrs
13[b]	C 200B	0.80	82 ± 1	0.622	-	-	17	167[a]
				0.612			20	
				0.505			139	
				0.490			142	
				0.440			161	
14[b]	C 200B	0.54	90 ± 2	0.680	-	-	18	161[a]
				0.665			21	
				0.630			48	
				0.490			141	
				0.295			160	

(a) Tests terminated because of diminished performance
(b) No polarization data taken

TABLE III

PRE-SINTERED MEMBRANE COMPOSITION AND PROCESSING TEMPERATURES

Sample No.	Pre-Sintered Composition ZrO_2	Pre-Sintered Composition H_3PO_4	Pre-Sintering Temp. (^oC)	Sintering Temperature (^oC)
A200A	70	30	200	300
A200B	70	30	200	500
A200C	70	30	200	800
A600A	70	30	600	300
A600B	70	30	600	500
A600C	70	30	600	800
B200A	60	40	200	300
B200B	60	40	200	500
B200C	60	40	200	800
B600A	60	40	600	300
B600B	60	40	600	500
B600C	60	40	600	800
C200A	50	50	200	300
C200B	50	50	200	500
C200C	50	50	200	800
C400A	50	50	400	300
C400B	50	50	400	500
C400C	50	50	400	800
C600A	50	50	600	300
C600B	50	50	600	500
C600C	50	50	600	800
C800A	50	50	800	300
C800B	50	50	800	500
C800C	50	50	800	800
D200A	40	60	200	300
D200B	40	60	200	500
D200C	40	60	200	800
D600A	40	60	600	300
D600B	40	60	600	500
D600C	40	60	600	800

(cont. next page)

TABLE III (CONT'D)

PRE-SINTERED MEMBRANE COMPOSITION AND PROCESSING TEMPERATURES

Sample No.	Pre-Sintered Composition ZrO_2	Pre-Sintered Composition H_3PO_4	Pre-Sintering Temp. (°C)	Sintering Temperature (°C)
E200A	30	70	200	300
E200B	30	70	200	500
E200C	30	70	200	800
E600A	30	70	600	300
E600B	30	70	600	500
E600C	30	70	600	800
H200A	75	25	200	300
H200B	75	25	200	500
H200C	75	25	200	800
H600A	75	25	600	300
H600B	75	25	600	500
H600C	75	25	600	800
I200A	80	20	200	300
I200B	80	20	200	500
I200C	80	20	200	800
I600A	80	20	600	300
I600B	80	20	600	500
I600C	80	20	600	800
J200A	85	15	200	300
J200B	85	15	200	500
J200C	85	15	200	800
J600A	85	15	600	300
J600B	85	15	600	500
J600C	85	15	600	800

published in the literature. The performance at ambient temperature is not quite as high as that obtained in the 60^{o} - $70^{o}C$ range for the same membrane (Tests 4, 5 and 8), but it is closer to the values obtained at $75^{o}C$ (Tests 10 and 11).

Tests 12, 13 and 14, conducted over the 80^{o} - $90^{o}C$ temperature range on the same type of membrane were characterized by frequent dips on performance level. It was possible to regain such losses by momentarily increasing the hydrogen and oxygen flow rates. It can be concluded that for the C200B as evaluated in the present fuel cell, a level of performance is attainaboe at temperatures as high as $90^{o}C$ and comparable to that found at a lower temperature. However, this level of performance is of shorter duration without proper fuel cell maintenance. It is our belief that this may be due to various factors such as

a. clogging of backup plates
b. flooding of catalyst pores
c. dehydration of the membrane.

Tests 6 and 7 were performed with the C200B membrane which had been impregnated with phosphiric acid three times and heated several hours in an oven at $120^{o}C$ after each impregnation. This procedure had effected little or no improvement in transverse strength. As will be shown below in Section 3.2 - Membrane Composition, Fabrication and Evaluation Studies, sintering at $500^{o}C$ after each impregnation with phosphoric acid is highly effective in increasing transverse strength. The results of Tests 6 and 7 show that the former phosphoric acid impregnation technique (without sintering at $500^{o}C$) affords no special promise. This is indicative that the main transport mechanism is probably related to bonded phosphate and that free H_3PO_4 does not contribute much to ion transport. Other evidence of this is that membranes from which free H_3PO_4 has been removed, run very well in fuel cell tests (See p. 3-8, last paragraph).

Tests 2 and 9 were performed with a C200B membrane treated with phosphoric acid as described for Tests 6 and 7, and in addition, impregnated with platinum black in the following manner. A mixture of the C200B pressing material was ball-milled with 10% by weight platinum black.

Then, the composite membrane from this material along with C200B material was pressed at 15 tons and sintered at 500°C for two hours. The product obtained is shown in Figure 1. What differentiates Test 2 from Test 9 is that in Test 9, additional platinum black was sprinkled on to the membrane surface (0.3 g on each side) just prior to the assembling of the membrane-electrode wafer configuration. This is the usual procedure for each test. The additional platinum was excluded from Test 2. Although initially the performance of Test 2 is signficantly less than that of Test 9, they become essentially equal after 200 hours of operation. The performance of Test 9 is approximately 20% higher than that obtained for the same membrane without platinum catalyst impregnation. In addition, the fuel cell resistance is at least one-fourth to one-thirdthe resistance of equivalent tests without impregnated platinum. Evidently, impregnation with platinum lowers membrane electrode contact resistance. The fact that fuel cell performance in Test 2 improves with test life, contrary to the usual behavior observed, may be due to the catalyst remaining well imbedded in the membrane matrix during that test. Loss of catalyst due to soaking of the membrane surface may be a leading cause for the diminishing performance with increasing test cell life usually found. Voltage vs. test duration curves at constant current density are given for Tests 2 and 9 in Figure 2, Test 13 in Figure 3 and Test 14 in Figure 4. Polarization curves for Tests 1, 2, 4, 5, 6, 7, 8, 9, 11 and 12 are given in Figures 5-14, inclusive.

At this point, it would appear that impregnation of the membrane with platinum catalyst followed by sintering offers a decided advantage in fuel cell operation. This would be helpful especially at higher test temperatures. This matter will be explored further in the near future, as will the aspect of incorporation of a higher concentration level of platinum by this technique.

The matter of fluctuating performance levels at temperatures in the 80° - 90°C range will be studied from the standpoint of the use of wet reactant gases in order to ascertain the causes thereof. Re-design of the electrode - backup plate configuration, rendering them less susceptible to flooding may improve the situation. Substitution of a better water-balancing agent than "Zeolon H" could prove beneficial, but not too much attention will be given to this aspect in view of the decision to concentrate on the fuel cell design and tests for the rest of the program.

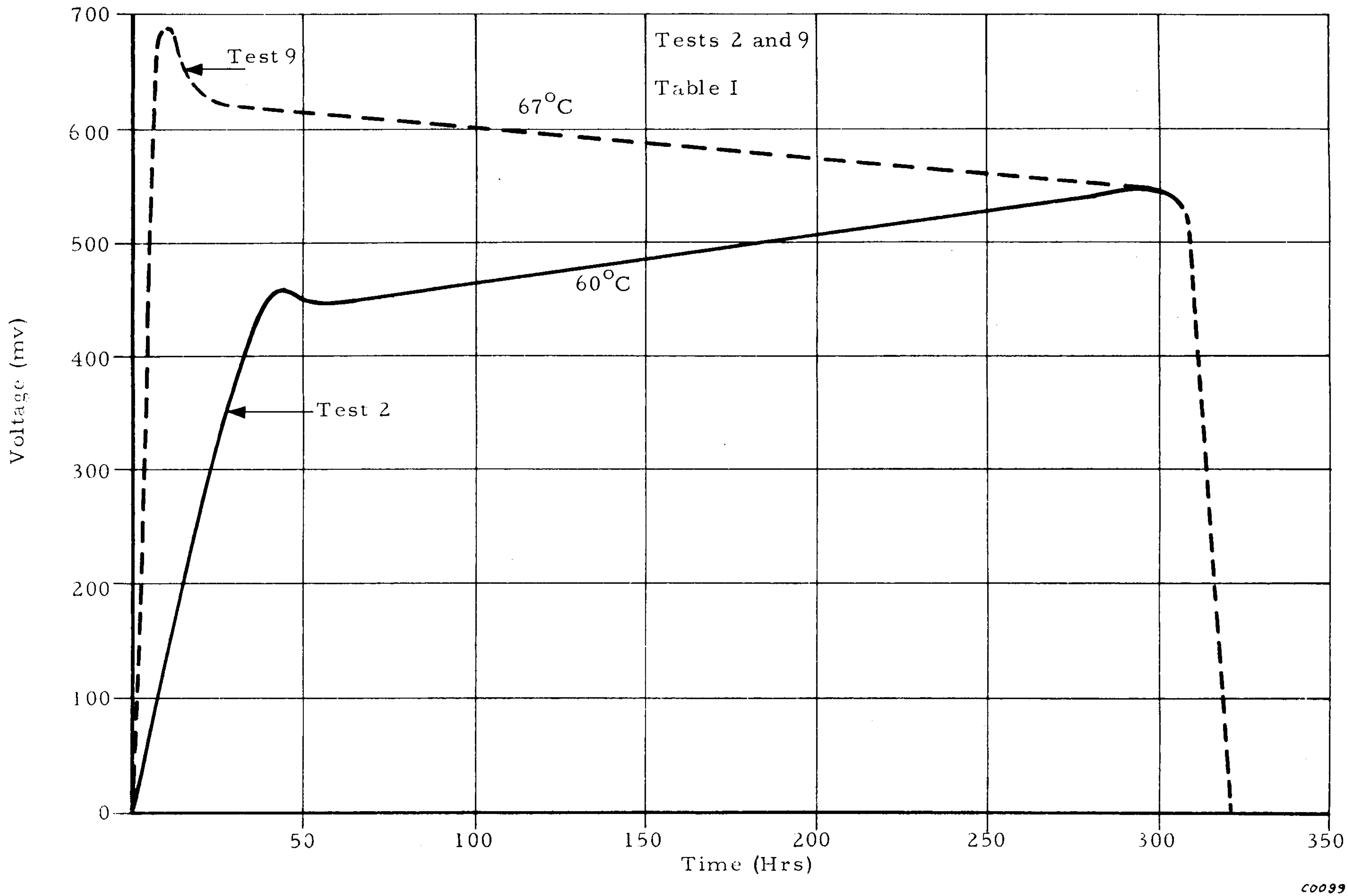
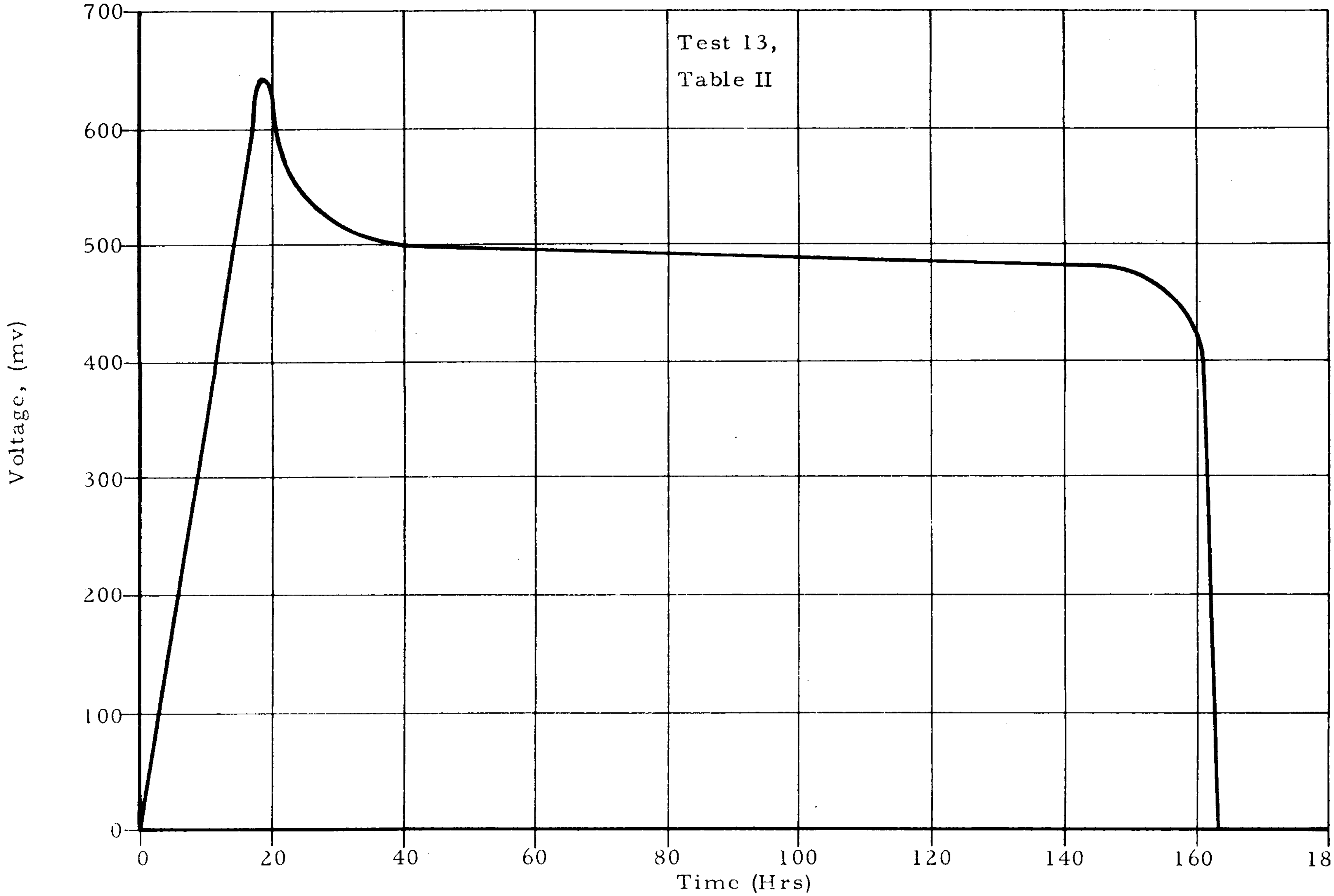


Figure 2. Synopsis of Life Tests Voltage;Versus Time at 30 ma/cm^2



Note: During this run water was extracted three times each day from test cell.

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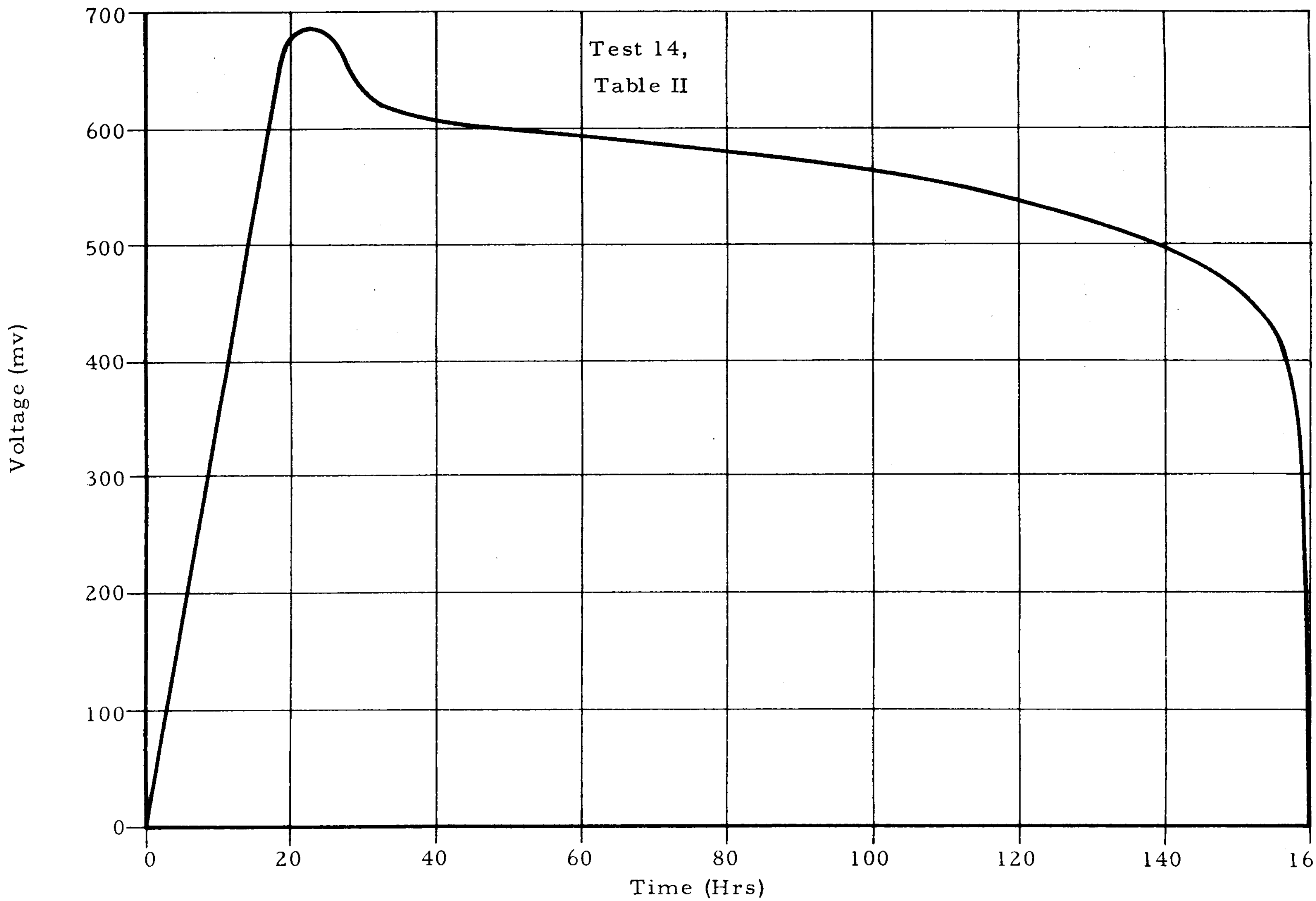
Figure 3. Synopsis of Life Tests Voltage;Versus Time at 82°C and 30 ma/cm^2



Note: During this run water was extracted three times each day from test cell

C0101

Figure 4. Synopsis of Life Tests Voltage Versus Time at 90°C and 30 ma/cm^2

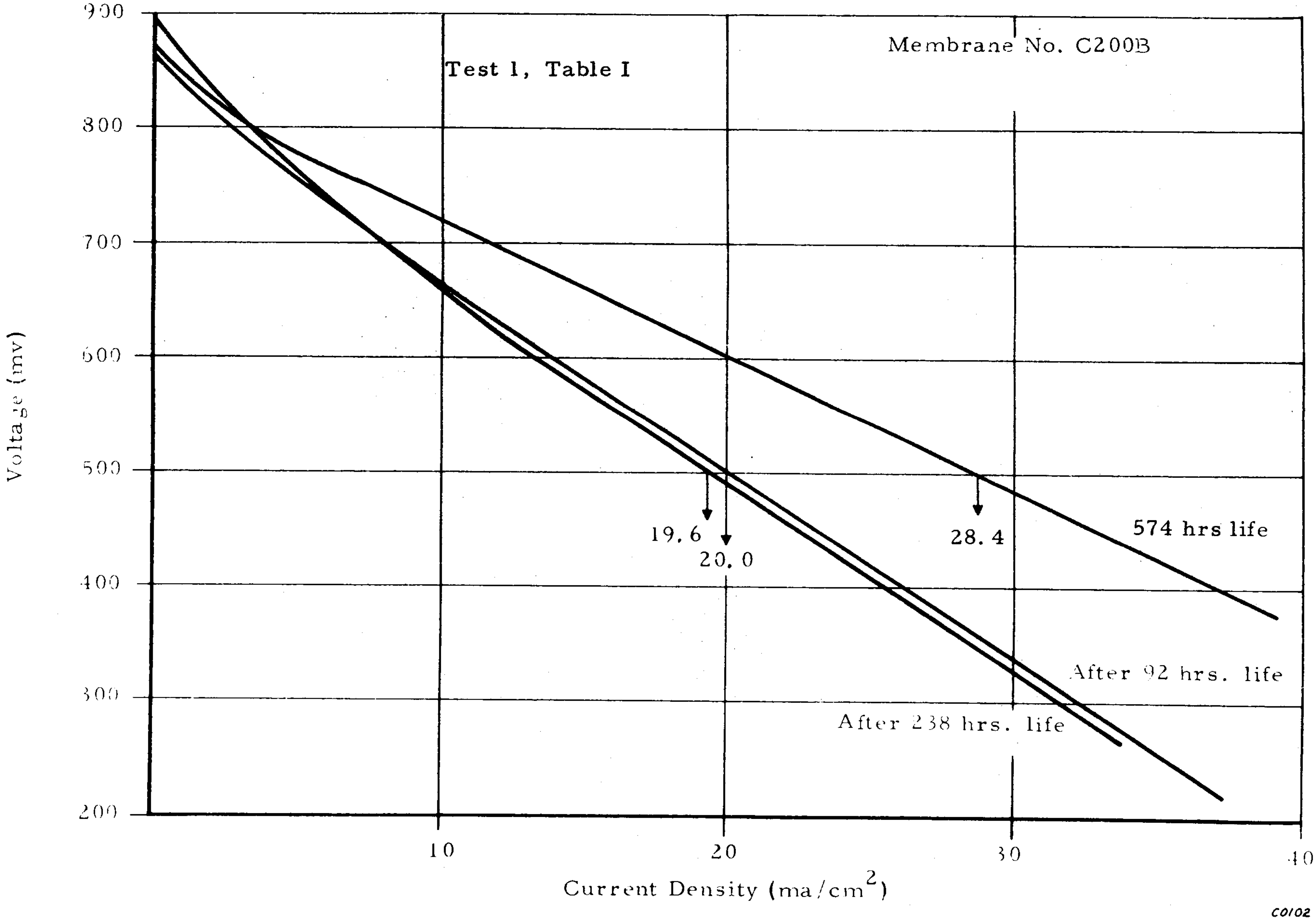


Figure 5. Polarization Curves for Inorganic Membrane Fuel Cell

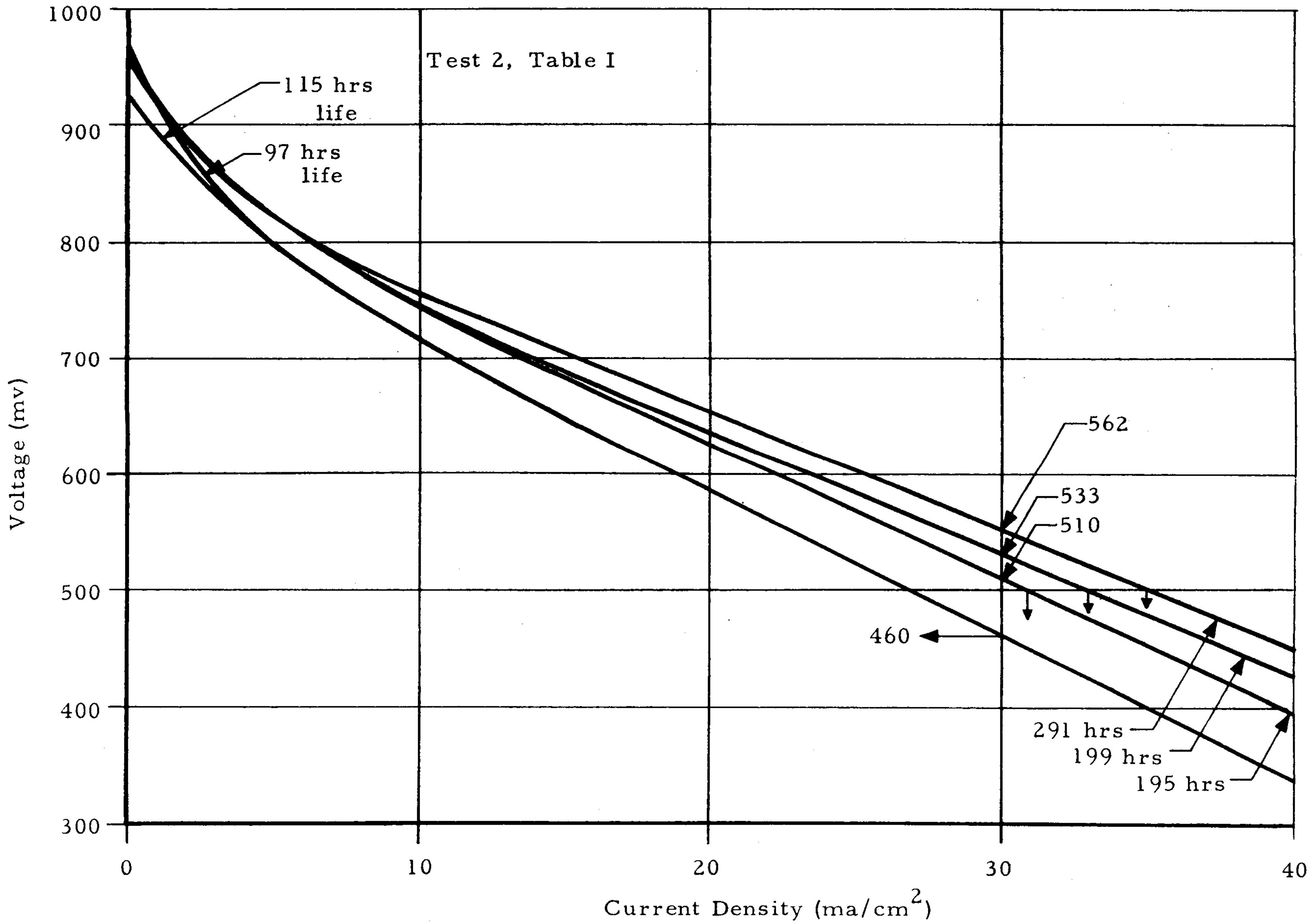


Figure 6. Polarization Curves for Inorganic Membrane Fuel Cell

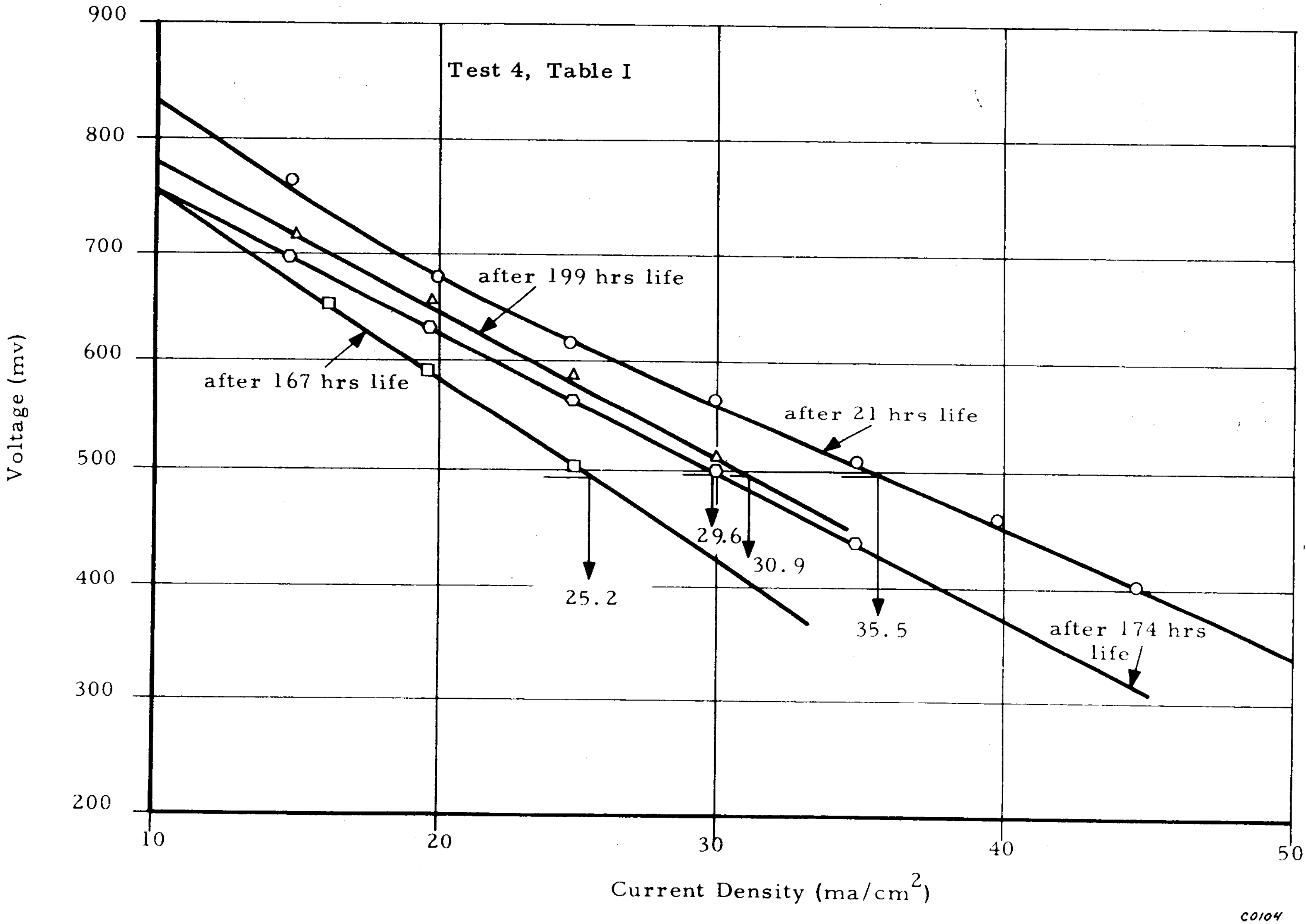
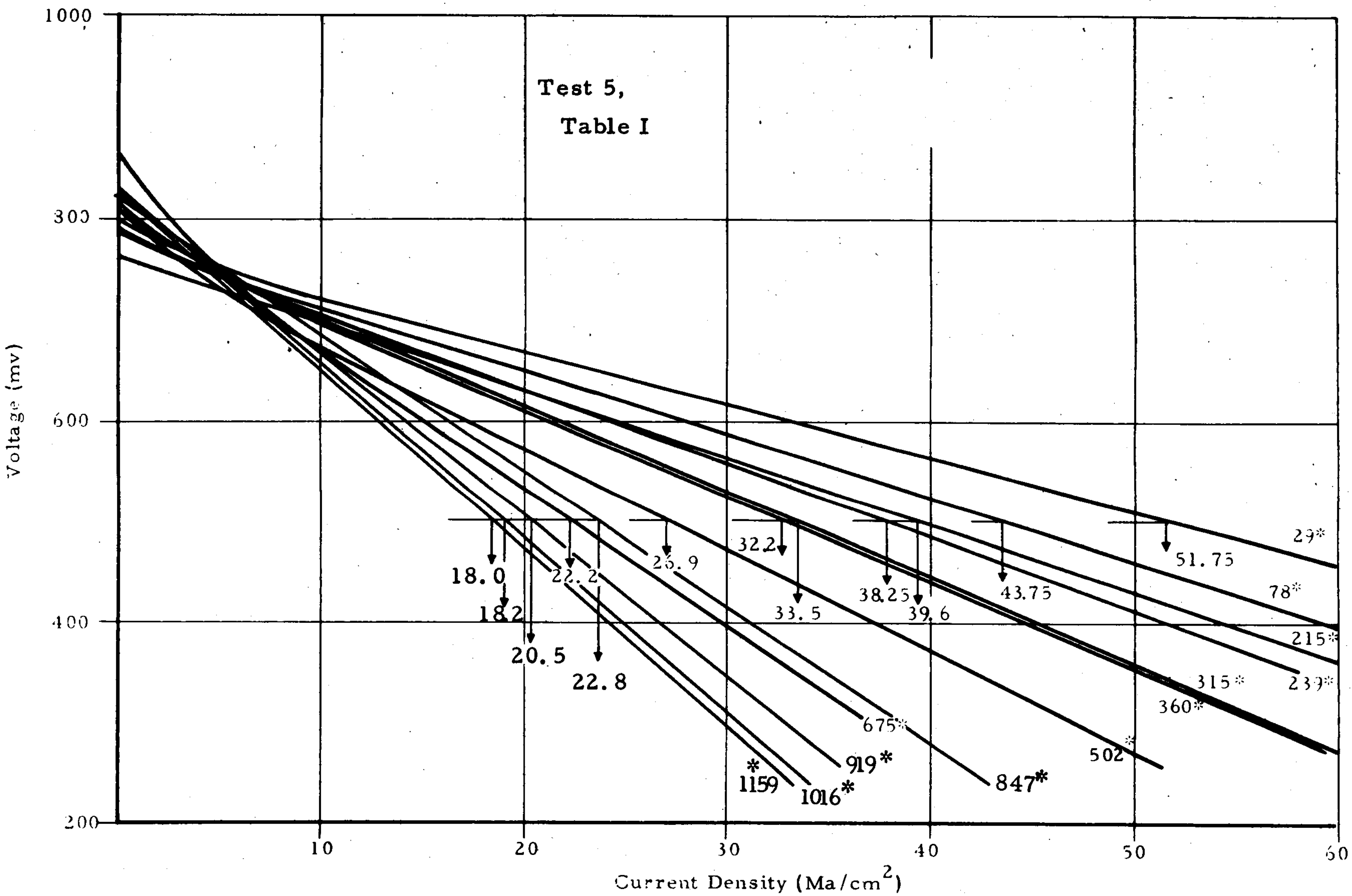


Figure 7. Polarization Curves for Inorganic Membrane Fuel Cell



* After indicated number of hours life.

C0105

Figure 8. Polarization Curves for Inorganic Membrane Fuel Cell

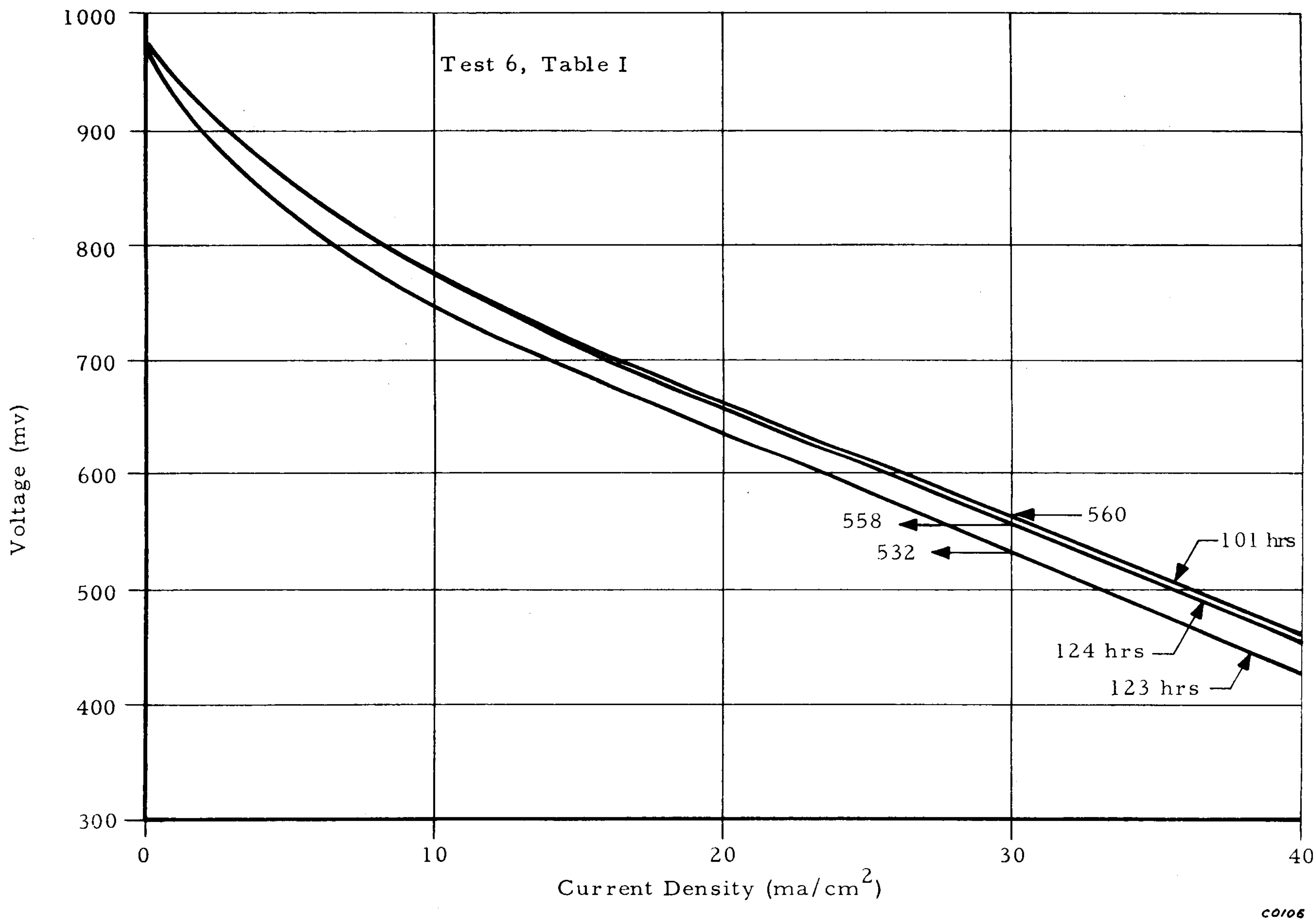


Figure 9. Polarization Curves for Inorganic Membrane Fuel Cell

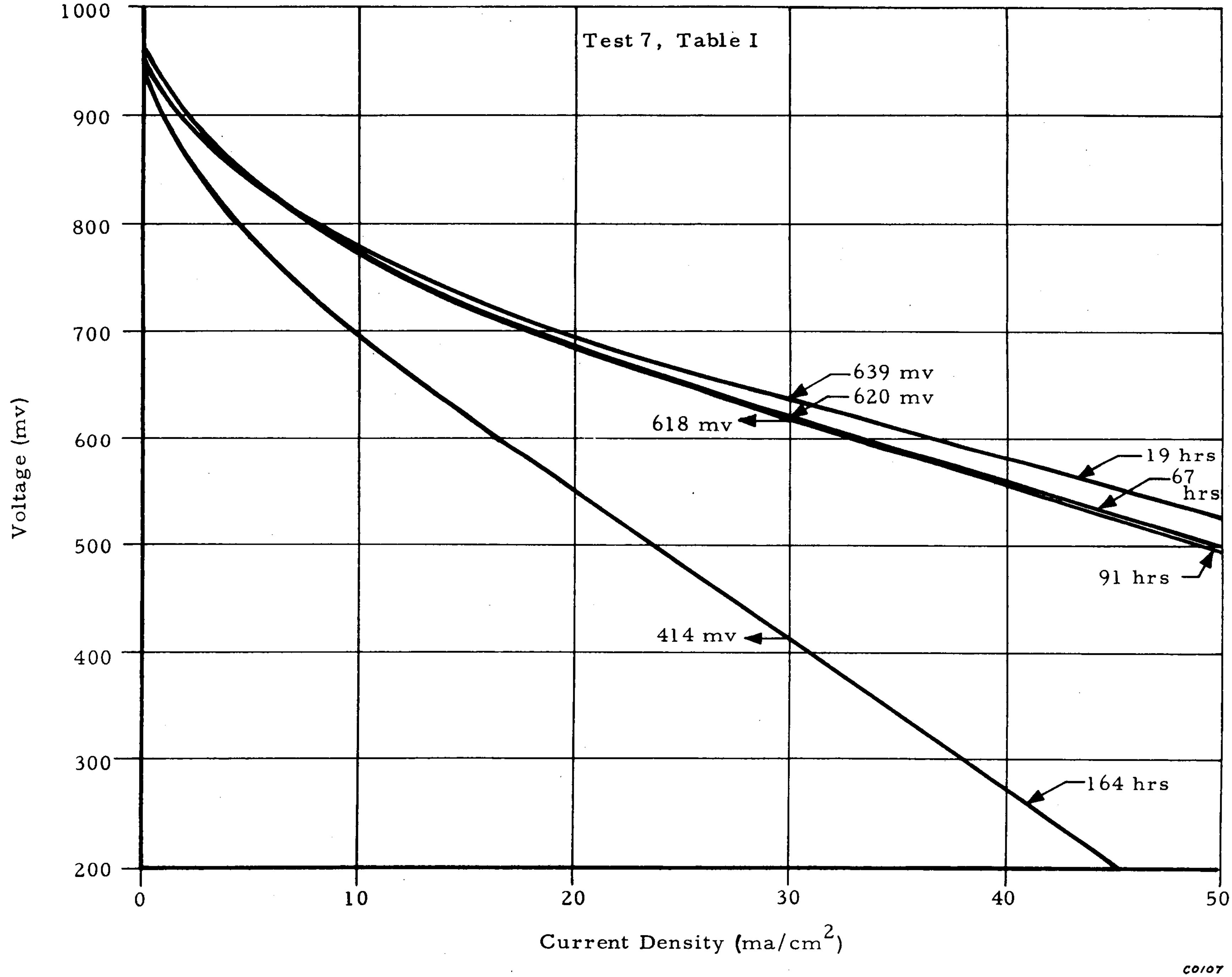
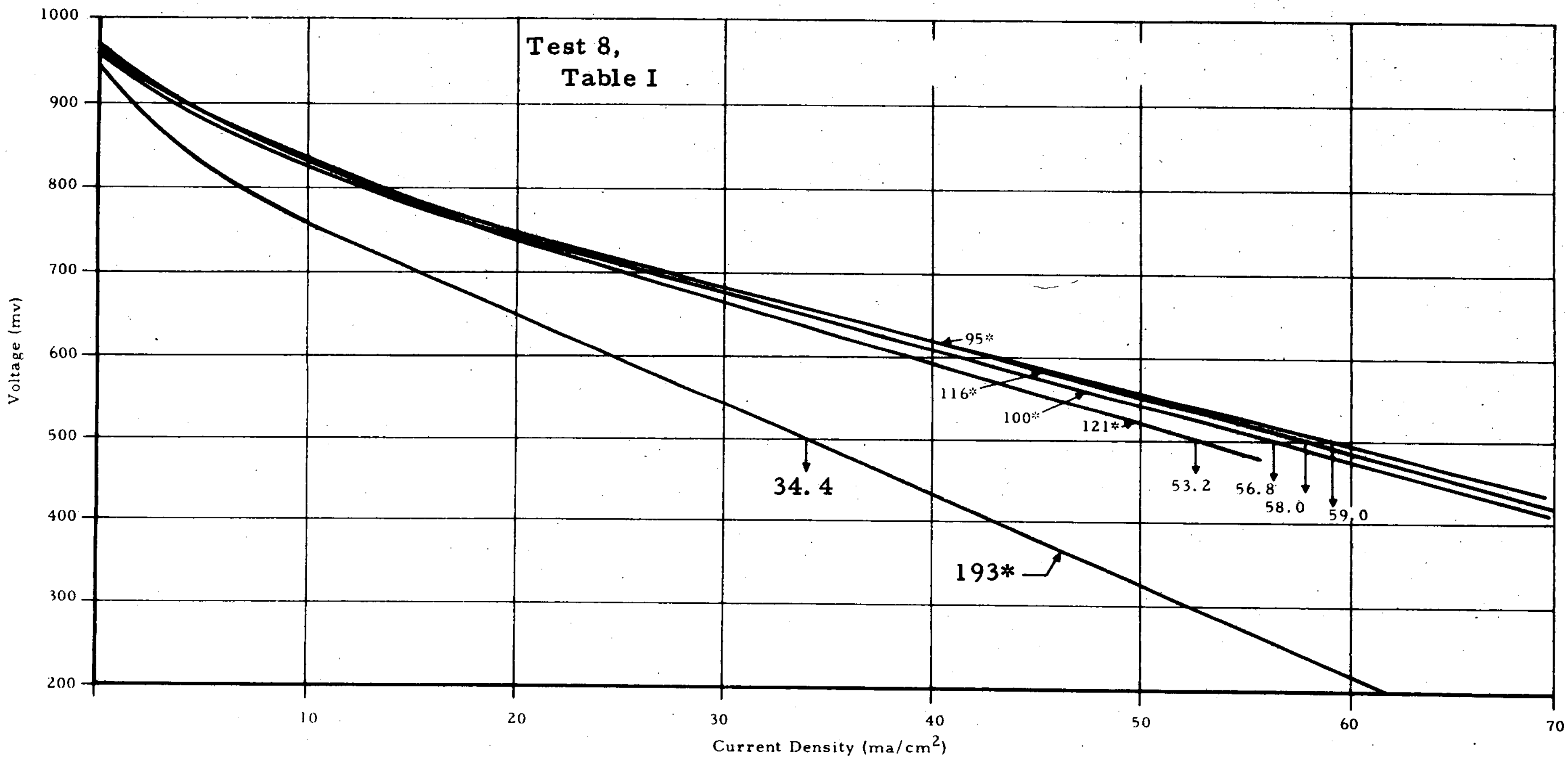


Figure 10. Polarization Curves for Inorganic Membrane Fuel Cell



* After indicated number of hours life.

C0108

Figure 11. Polarization Curves for Inorganic Membrane Fuel Cell

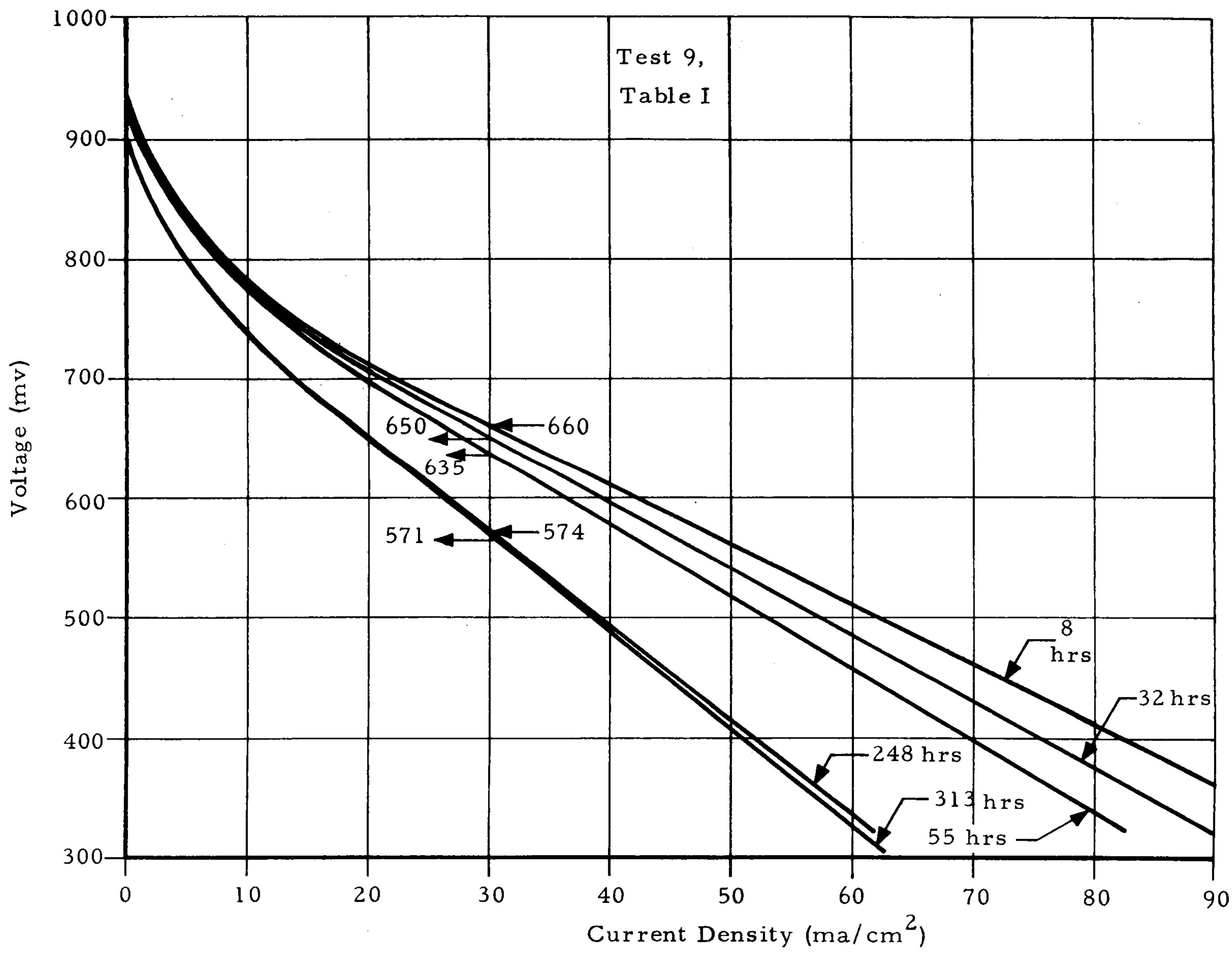
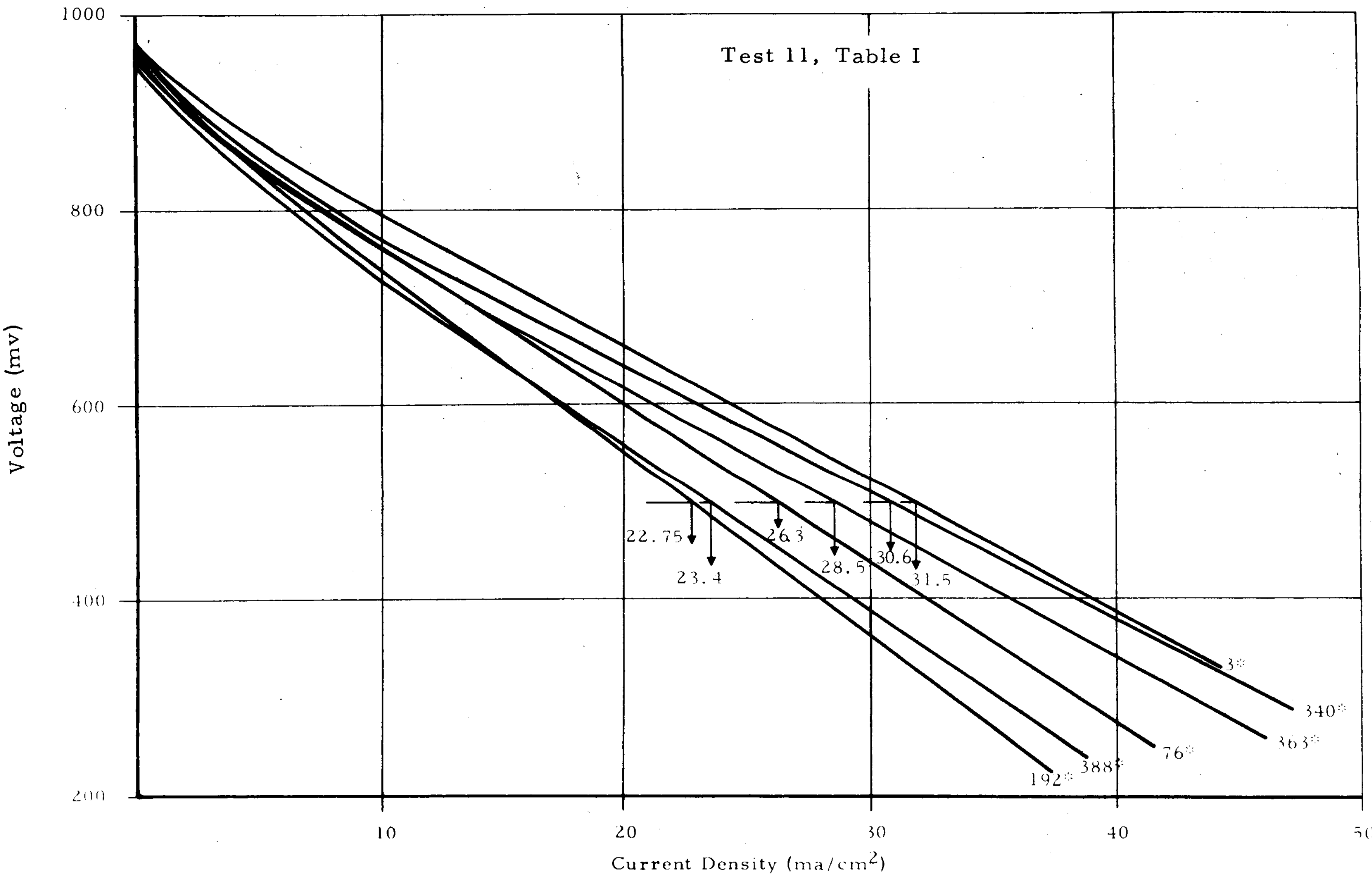


Figure 12. Polarization Curves for Inorganic Membrane Fuel Cell



* After indicated number of hours life.

C0110

Figure 13. Polarization Curves for Inorganic Membrane Fuel Cell

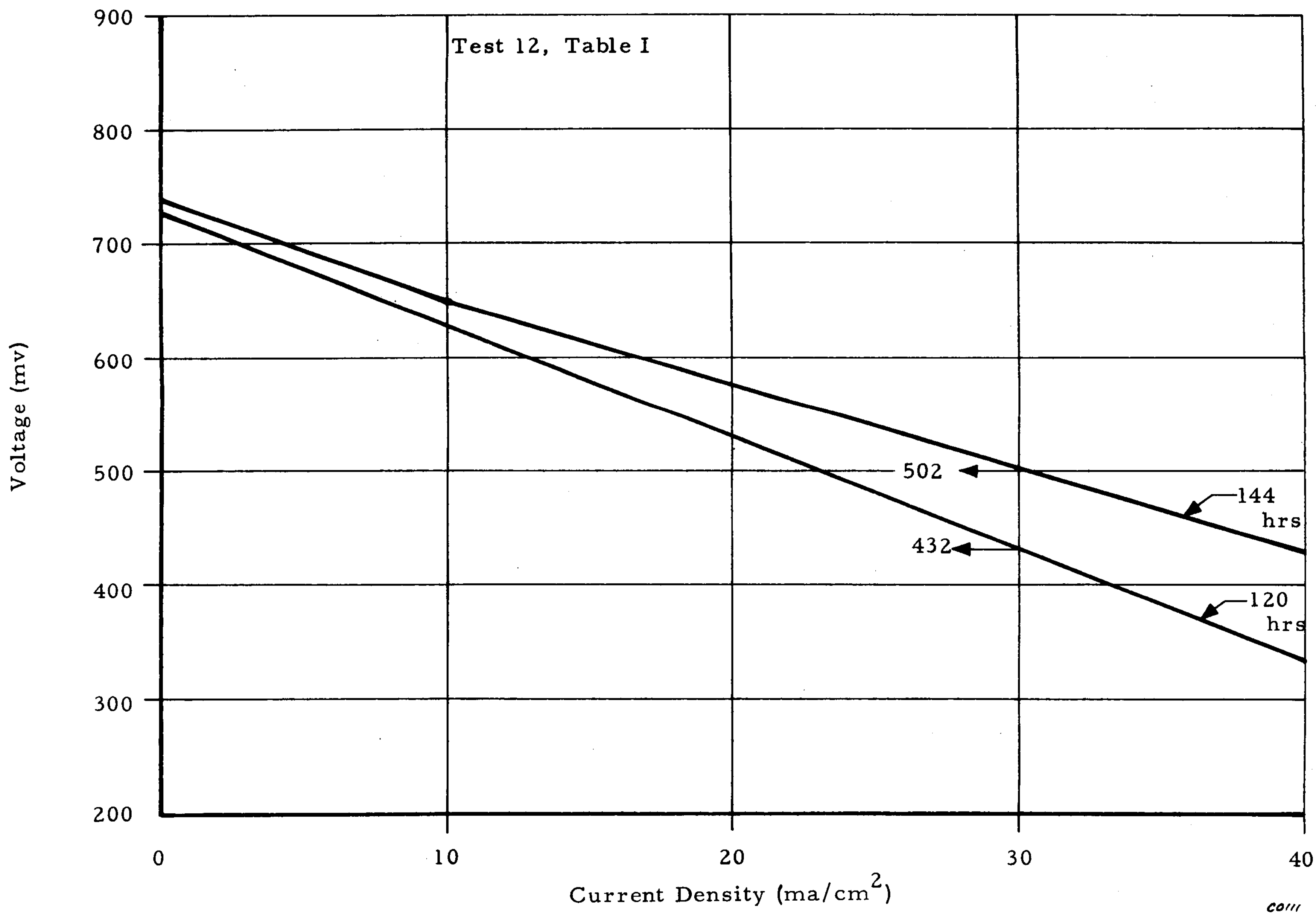


Figure 14. Polarization Curves for Inorganic Membrane Fuel Cell

3.2 Membrane Composition, Fabrication and Evaluation Studies

The program plan as outlined in the previous Quarterly Report and extended in Monthly Progress Reports for October and November[3,4] can be summarized as follows:

Membranes were prepared in the following manner. An initial mixture of TAM c.p. ZrO_2 and H_3PO_4 were prepared at ratios varying from 85/15 to 30/70 and sintered at temperatures levels of 200°C and 600°C. In one instance, i.e., the 50/50 mixture sintering was performed at 400°C and 800°C as well. These presintered materials were crushed and ground to minus 80 mesh and mixed with equal parts of H_3PO_4 and "Zeolon H". Then, they were dried for 16 hours at 130°C and granulated to minus 32 plus 80 mesh. Next, they were pressed at 15 tons load into 2-inch diameter membranes having a thickness of the order of 0.7 mm and finally, they were sintered at temperatures of 300°, 500° and 800°C for two hours.

The various membrane compositions prepared and corresponding processing temperatures are listed in Table III. During the current report period the preparation and evaluation of these membranes were completed. The evaluation consisted of transverse strength, resistivity and hydrolytic stability studies. The significant results and correlations follow.

3.2.1 Transverse Strength Studies

Measurements were made by the procedure given in Reference 1. Plots of transverse strength versus percent zirconia in the presintered mixture are given in Figures 15 and 16 for the systems presintered at 200°C and 600°C, respectively. Maximum transverse strengths of 5,000 - 5,500 psi occur when the concentration of zirconia in the presintered mixture is 50% and in addition, at the 80-85% level.

It was possible to effect an increase in transverse strength to as high as 9520 psi in the high zirconia content membrane systems (H,I and J) by application of the following technique to the sintered membranes. These membranes were saturated with 85% phosphoric acid, oven dried at 110°C for two hours to remove the moisture introduced by the 85% phosphoric acid and sintered for five minutes at 500°C. The procedure was repeated three times. Transverse strengths obtained after the first and third impregnation are given in Table IV, wherein the percentage increase in phosphoric acid content after the first and third impregnation is included. It is planned to evaluate the higher strength membranes more extensively in a fuel cell at a later date.

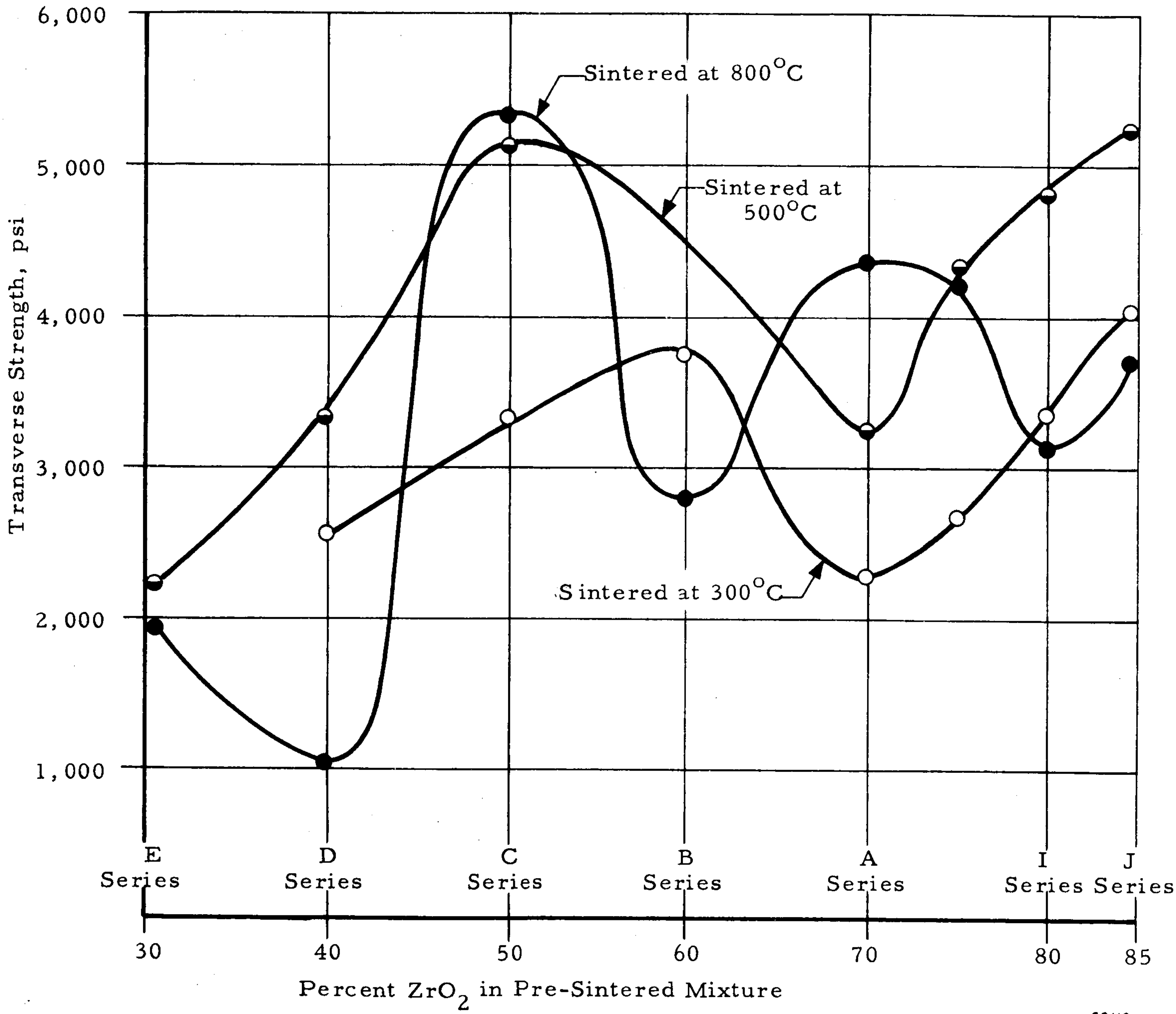


Figure 15. Transverse Strength Versus %ZrO_2 in Pre-Sintered Mixtures at 200°C and Indicated Sintering Temperatures

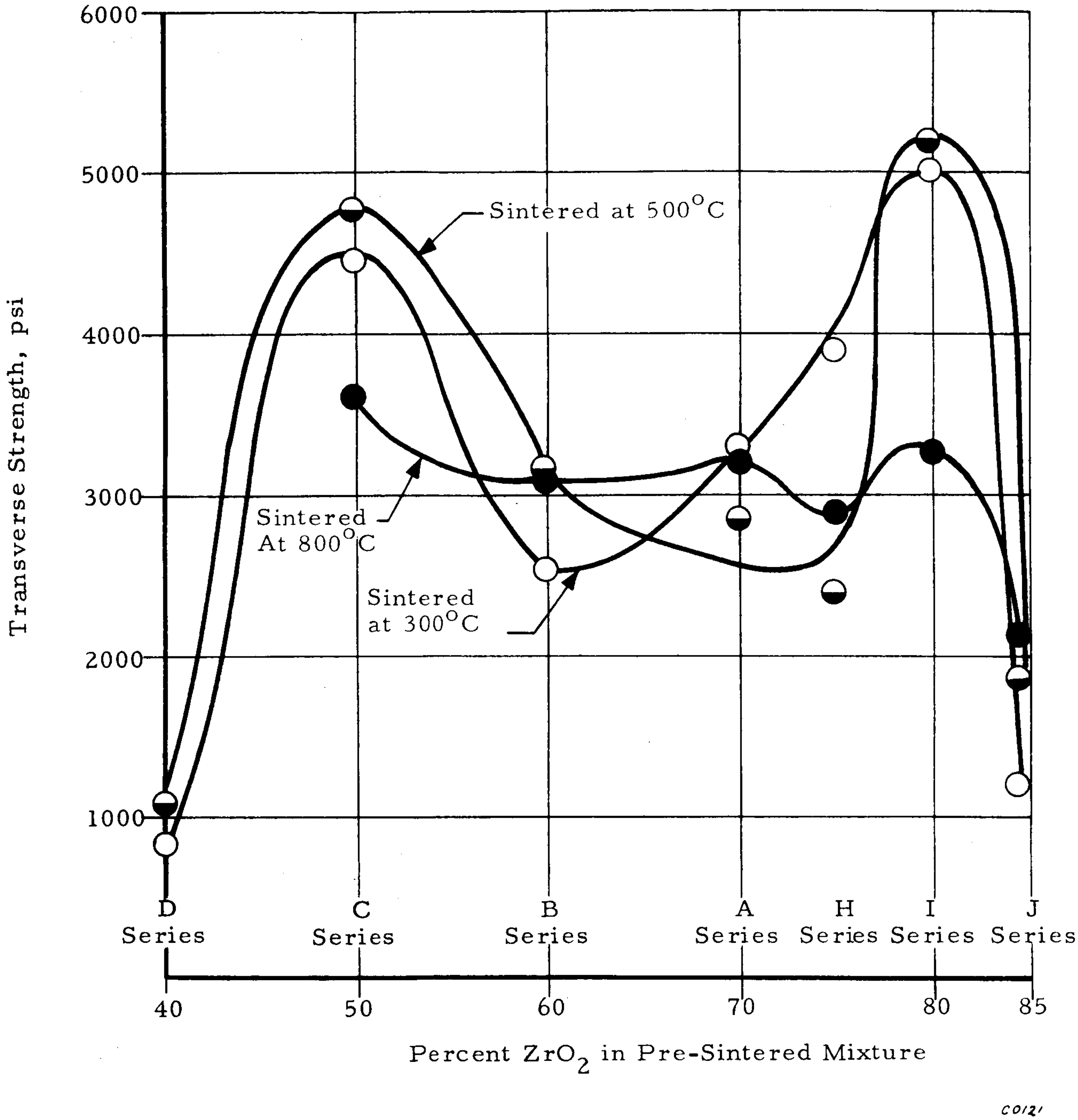


Figure 16. Transverse Strength Versus Percent ZrO_2 in Pre-Sintered Mixtures at 600°C and Indicated Sintering Temperatures

TABLE IV

EFFECT OF IMPREGNATION BONDING ON THE TRANSVERSE STRENGTH OF SINTERED FUEL CELL MEMBRANES

Sample No.	Modulus of Rupture (psi)	Modulus of Rupture 1st Imp (psi)	Modulus of Rupture 3rd Imp (psi)	H_3PO_4 Absorbed (%)
H200A	2680	4300	6750	19.0
H200B	4350	4900	7600	23.8
H200C	4280	5100	9520	28.5
H600A	3900	4620	5380	20.1
H600B	2400	5100	6140	40.4
H600C	2860	3640	4300	48.5
I200A	3380	4100	4700	19.9
I200B	4800	5000	6180	23.8
I200C	3150	5200	6400	35.5
I600A	2720	3270	4380	35.3
I600B	3400	4970	6760	38.2
I600C	2870	4570	5900	52.3
J200A	4040	4800	5640	18.4
J200B	5250	5340	6380	26.6
J200C	3700	7950	6450	32.0
J600A	1200	2900	6920	44.2
J600B	1850	2950	7050	37.0
J600C	2100	3200	7500	40.0
*I200B	4610	4820	8100	32.6

*Membrane Composition 1/0.5/1 pre-sintered material/H_3PO_4/Zeolite

3.2.2 Resistivity Studies

Measurements on the membranes listed in Table III were completed during this report period. Most of the pertinent data have been reported in the previous Quarterly Report and in the Monthly Progress Reports for October and November[3,4]. Resistivities were obtained at 70°, 90° and 105°C for relative humidities ranging from 26 to 83% by the procedure given in Reference 1. Test membranes were held between platinum electrodes having approximately 1.0 cm^2 surface area. The membrane electrode assembly was placed in a furnace maintained at one of the selected temperatures. Humidity was controlled by the flow of humidified nitrogen of accurately known moisture content. The resistivity was calculated from the membrane resistance measured by means of an alternating current bridge circuit at 1,000 cps. The resistivity values obtained are not included herein. Significant correlations are given, instead.

Generally, at sintering temperatures $\leq$ 500°C resistivities do not vary in any consistent manner with increase in zirconia concentration in the presintered mixture. However, at sintering temperatures of 800°C, the trend is definite, i.e., resistivities increase with increasing zirconia concentration. Plots of logarithm of resistivity versus percent relative humidity at 90°C for various membrane compositions presintered at 200°C and sintered at 500°C are given in Figure 17.

It has been noted throughout this study that presintering temperatures of the initial zirconia-phosphoric acid mixture have little or no effect on resistivity. However, sintering temperatures of the final mixture with phosphoric acid and "Zeolon H" do affect resistivity, that is, the resistivity increases with increasing sintering temperature. The largest enhancement of resistivity occurs when the sintering temperature increases from 500° to 800°C.

So far, in the current program, membranes of the system comprised of zirconia and phosphoric acid in 50/50 weight ratio in the presintered mixture have been evaluated exclusively in the fuel cell. An extensive analysis of the resistivity - humidity - temperature characteristics for this membrane system has been made. As typified by the plots of Figures 18, 19 and 20, resistivity decreases relatively little with increasing

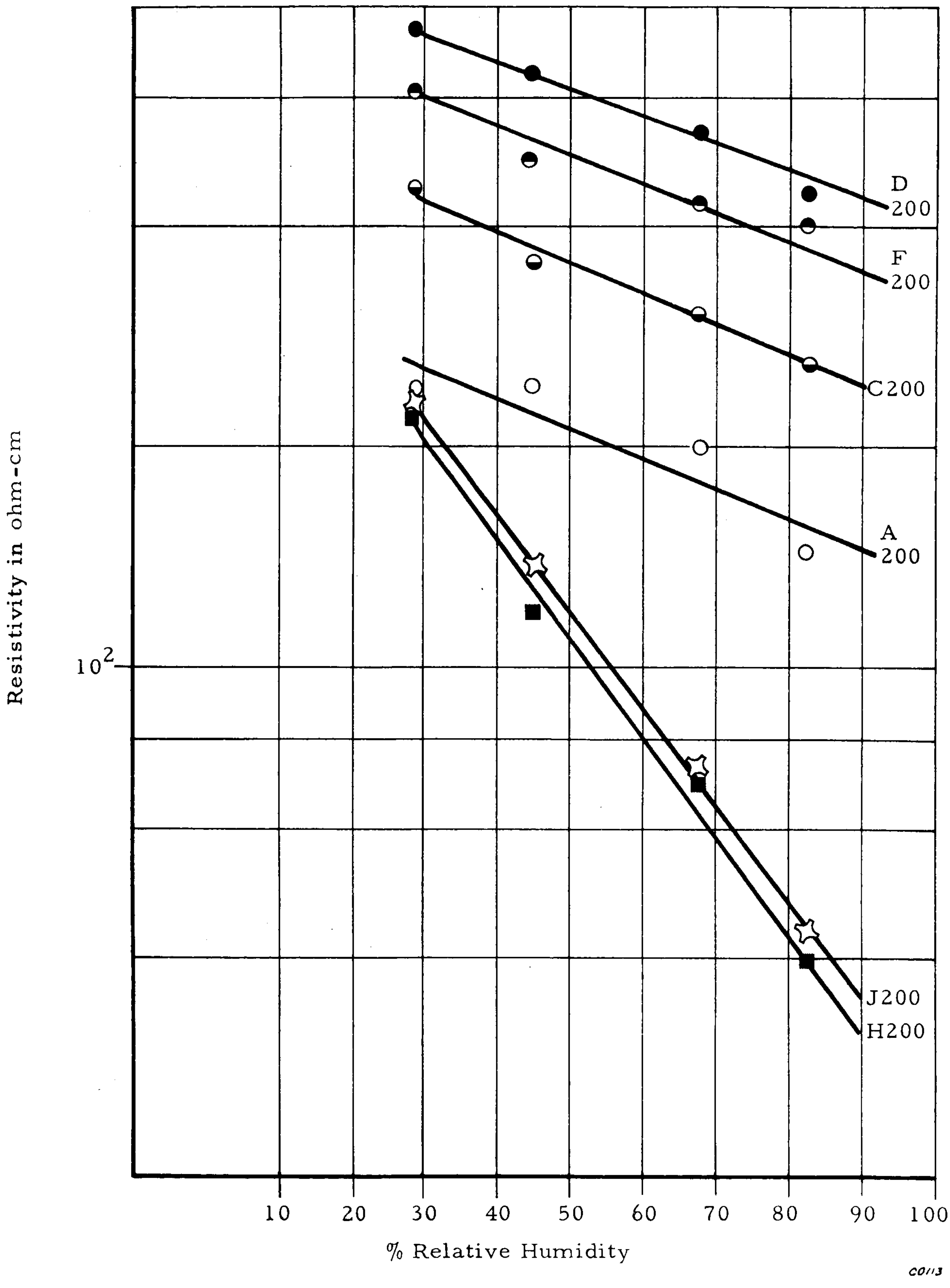
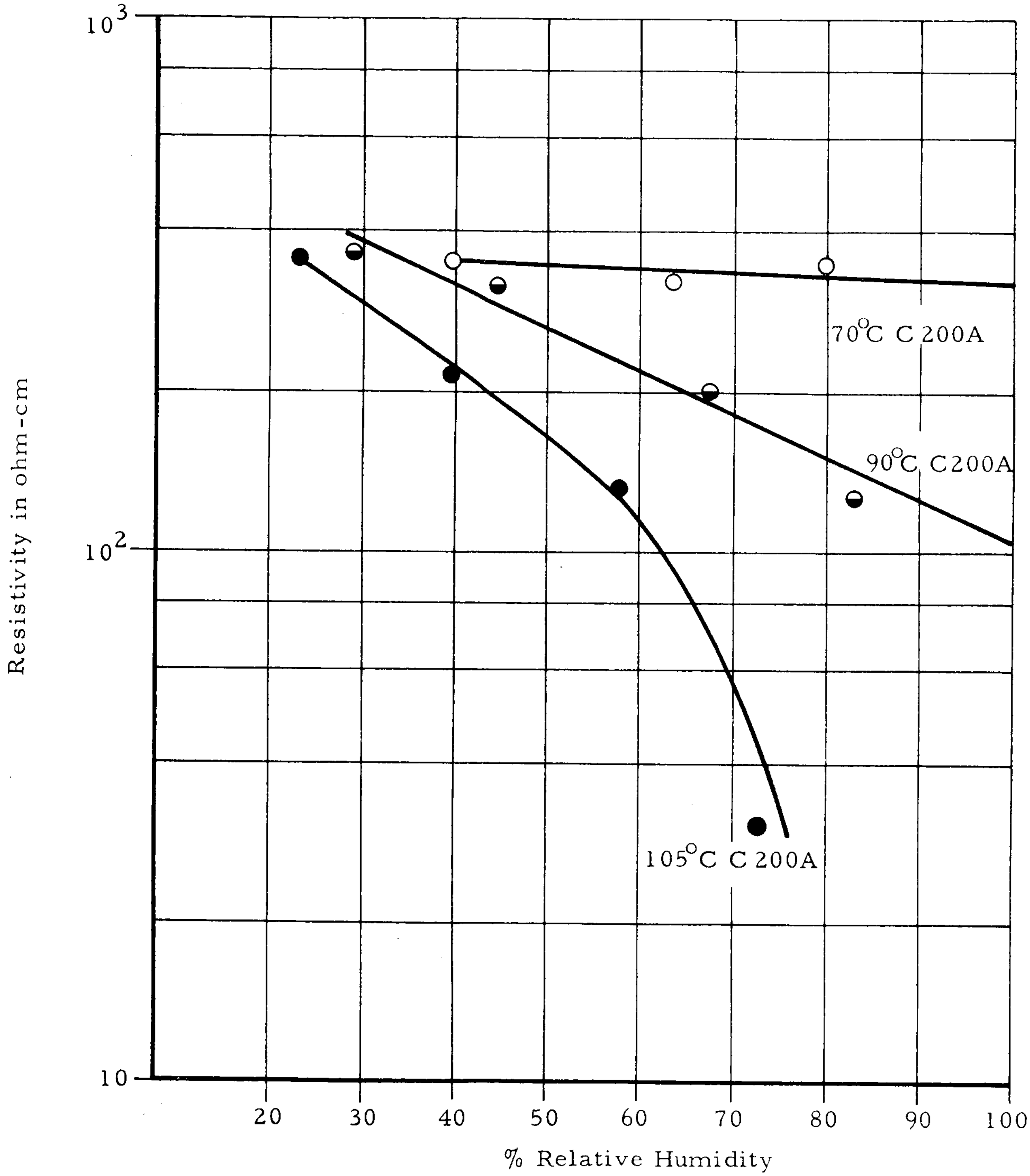


Figure 17. Log Resistivity Versus % Relative Humidity for Membrane Systems Pre-Sintered at 200°C and Sintered at 500°C–Measured at 90°C



C0114

Figure 18. Log Resistivity Versus Percent Relative Humidity for the C 200A Membrane at 70°, 90° and 105°C

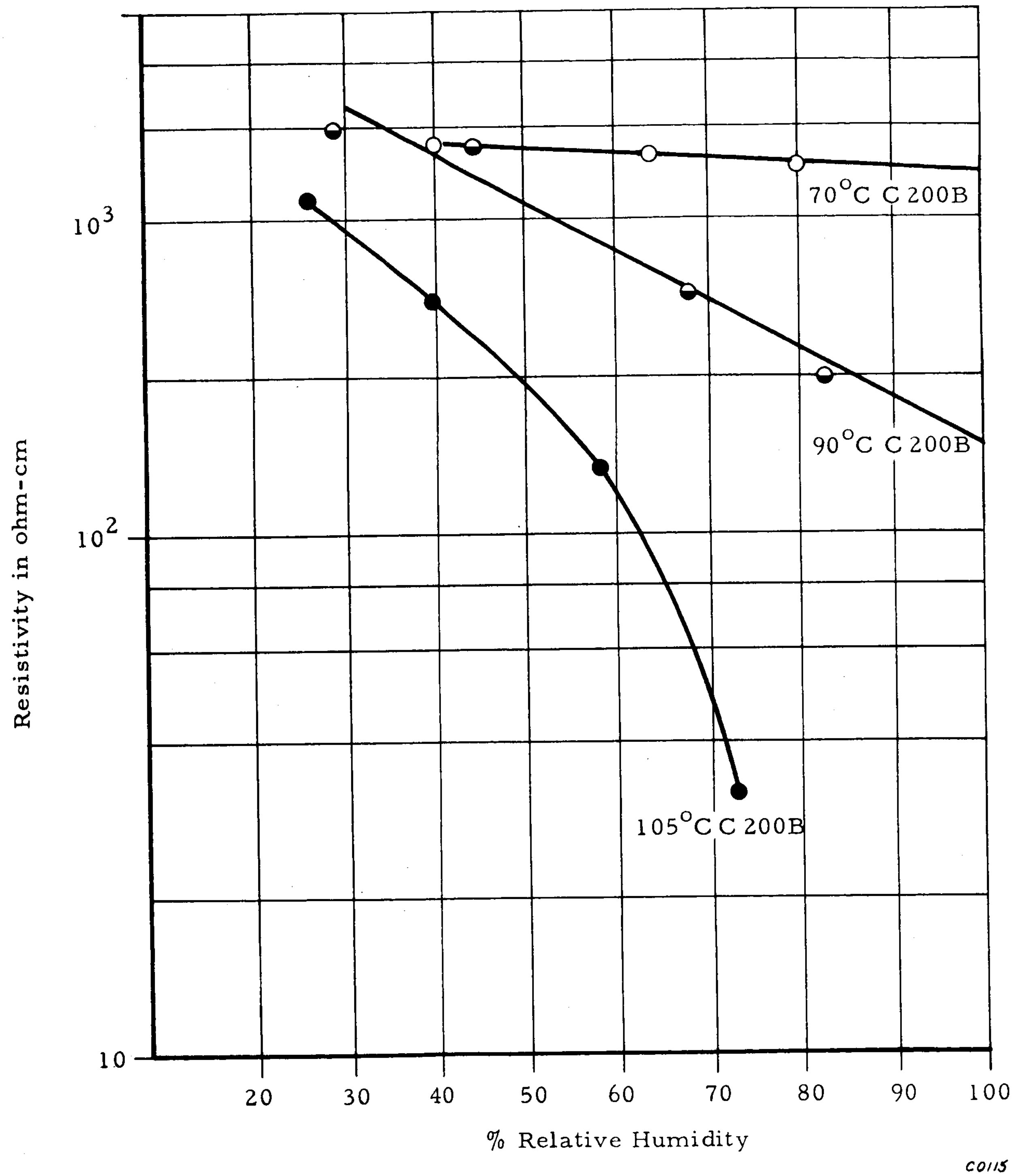


Figure 19. Log Resistivity Versus Percent Relative Humidity for the C 200B Membrane at 70°C, 90°C and 105°C

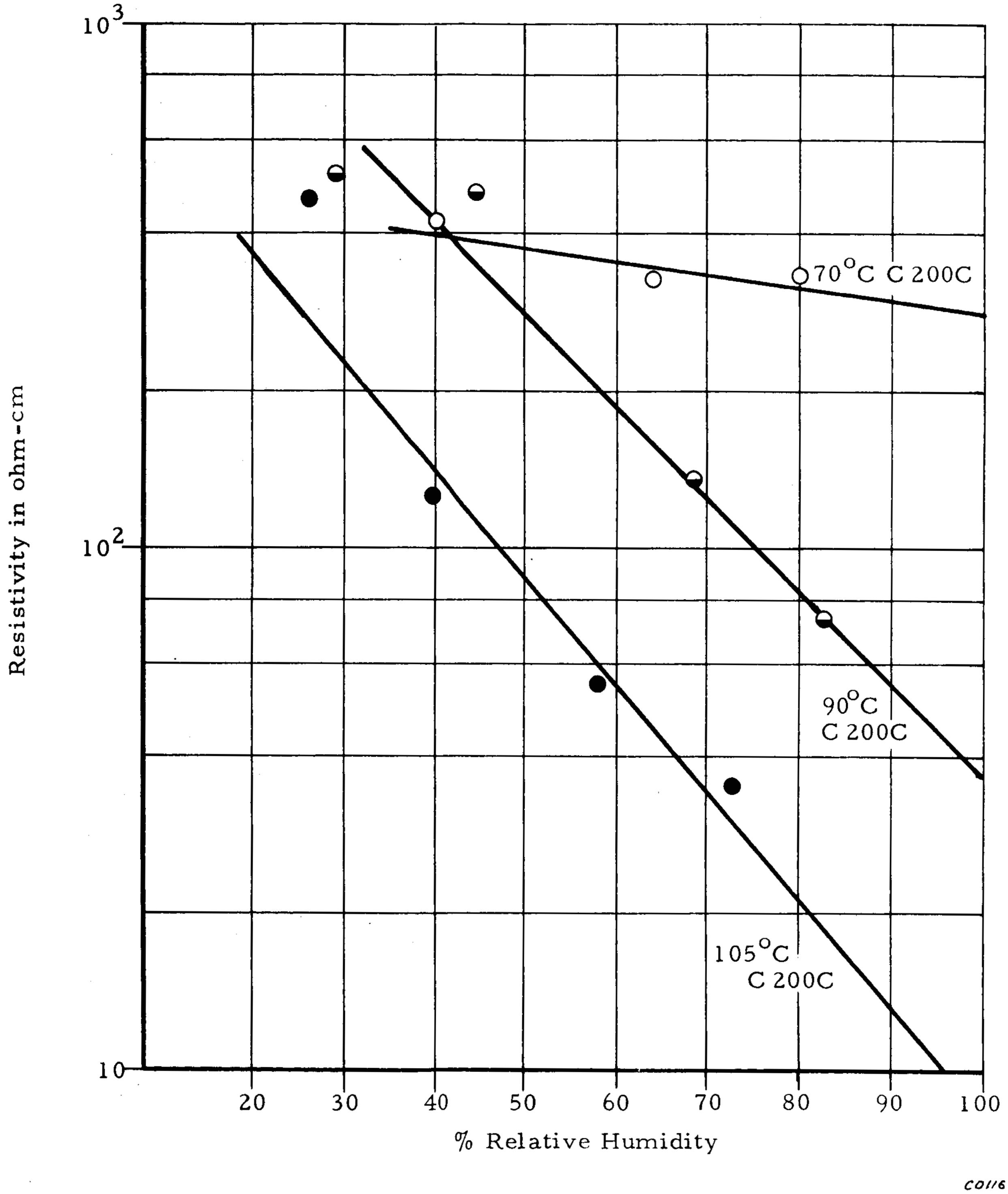


Figure 20. Log Resistivity Versus % Relative Humidity for C 200C Membrane at 70°C, 90°C and 105°C

relative humidity at 70°C; however, this variation becomes distinctly more pronounced at higher membrane temperatures. In addition, these plots demonstrate that the resistivities of membranes sintered at higher temperatures decrease more rapidly with increasing relative humidity.

In Figures 21, 22 and 23, are given the Arrhenius plots of logarithm of the resistivity versus the reciprocal of the absolute temperature for the C200 membranes at 50%, 70% and 90% relative humidity, respectively. The 90% relative humidity plots were taken from the extrapolation of the plots of Figures 18, 19 and 20. Activation energies were calculated from the slopes of the lines between 70°and 90°C ($1/T\ ^{\circ}K = 2.75 \times 10^{-3}$ - 2.92×10^{-3}) from these plots as well as those for the other membranes of the C- series. The results are given in Table V. At 50% relative humidity, the activation energies are in the 3-5k cal/mol range and at 70% relative humidity, they are in from 5 to 9k cal/mol. Finally, at 90% relative humidity, activation energies are in the 8-20 k cal/mol range.

Since the conductivity of the membranes improves significantly with increasing humidity and temperature, then improved fuel cell performance should be possible with these membranes under such conditions. This matter will be considered in future fuel cell designs. Under present fuel cell operating conditions, the environment of the membrane is evidently not the same as it was during this conductivity study at comparable temperatures.

3.2.3 Hydrolysis Studies

The investigation of the physical and chemical characteristics of the membrane material under fuel cell conditions is an integral part of this program. A substantial effort was devoted to this matter during the current report period in order to essentially complete this aspect of the program. In one series of experiments, the stability of the membranes listed in Table III in hot aqueous media were measured in the following manner. Two-inch membrane samples were each immersed under 200 ml of distilled water with agitation at 73°- 75°on a steam bath. Immersion periods were for two one-hour periods. After each immersion period, the aqueous phase was quantitatively transferred to a 250-ml volumetric flask, diluted to volume and potentiometrically titrated against 0.1 N sodium hydroxide standard

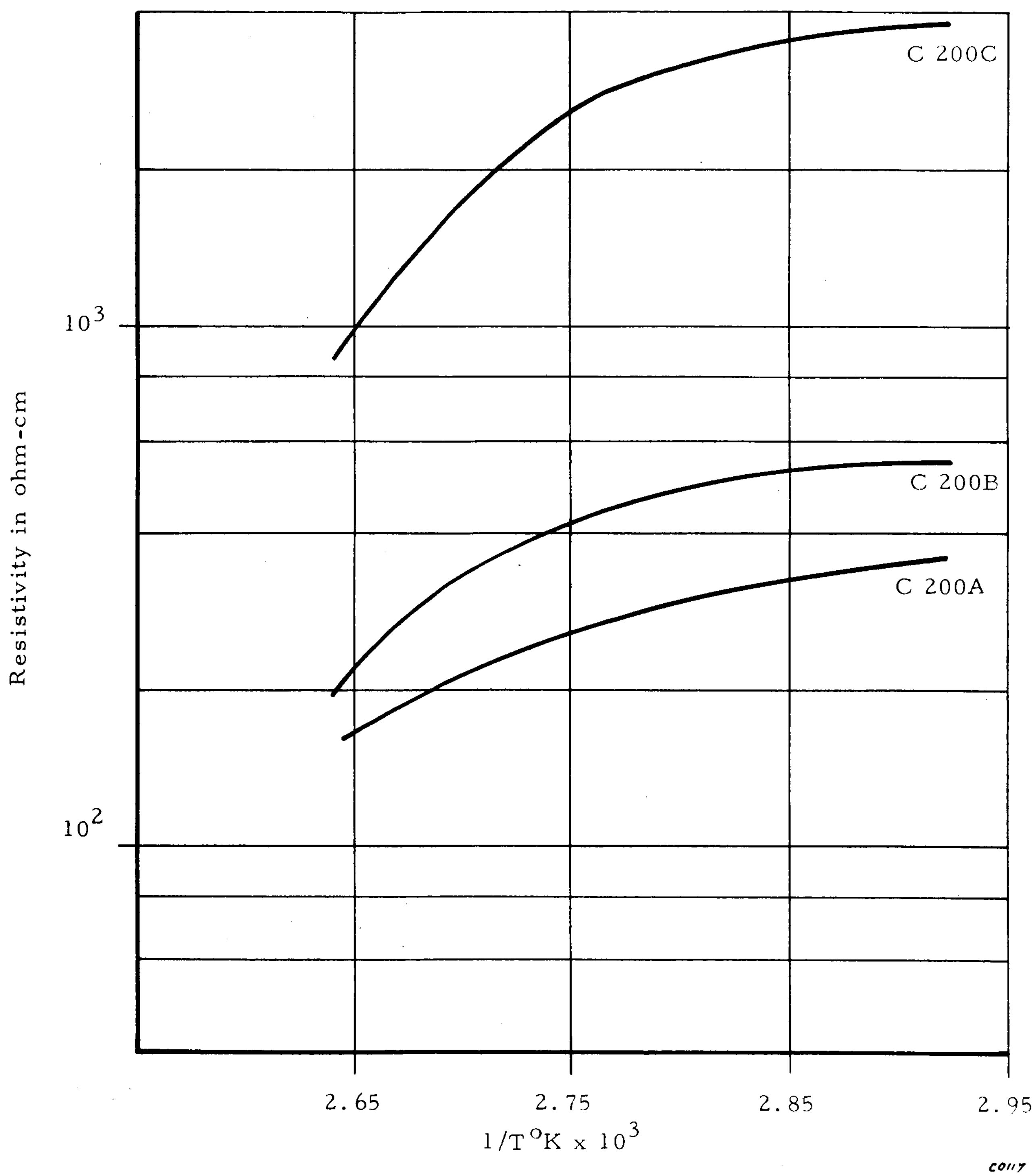


Figure 21. Arrhenius Plot of Log Resistivity vs $1/T\,^{o}K$ for the C 200 Membranes at 50% Relative Humidity

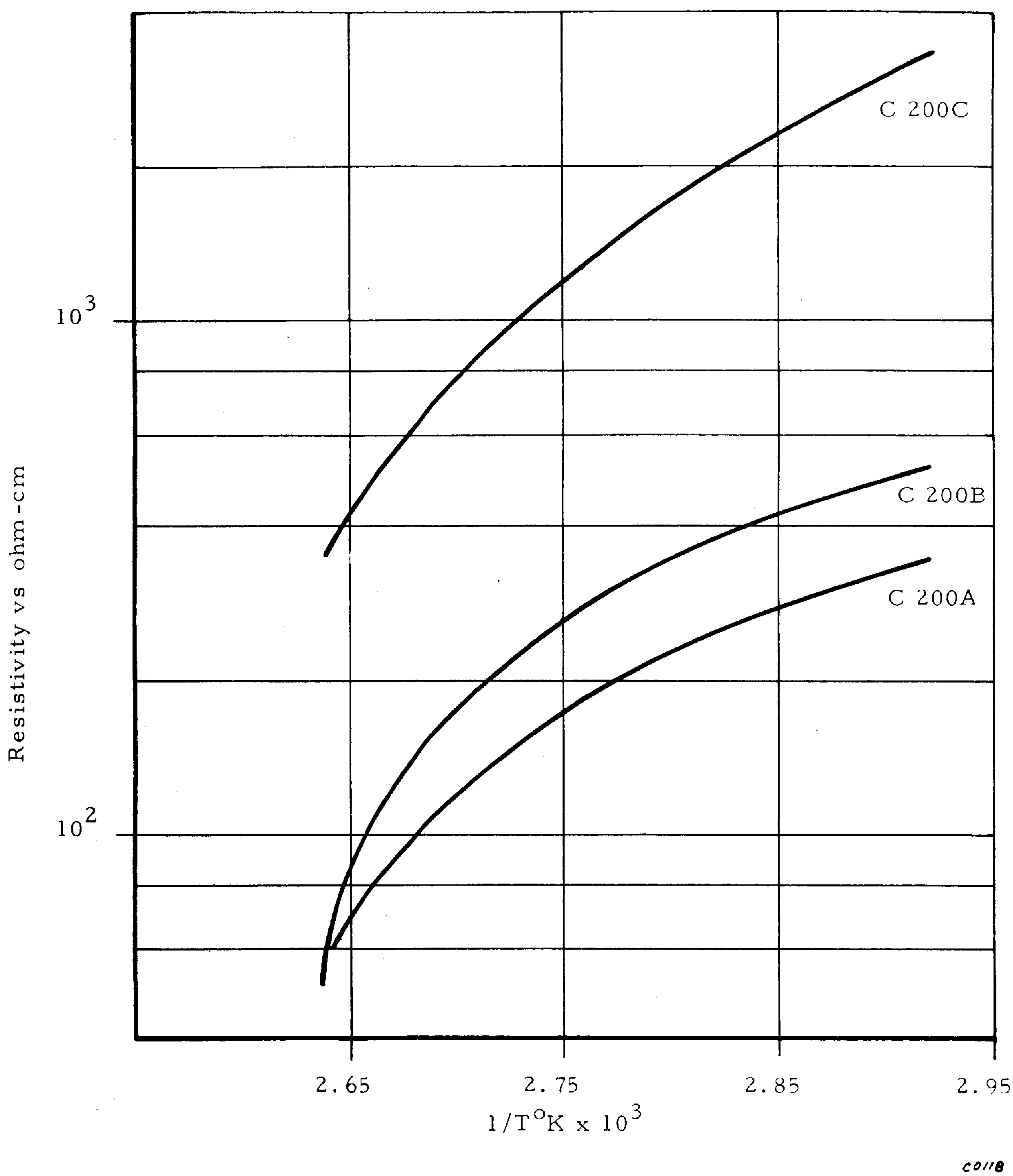


Figure 22. Arrhenius Plot of Log Resistivity vs $1/T^oK$ for the C 200 Membranes at 70% Relative Humidity

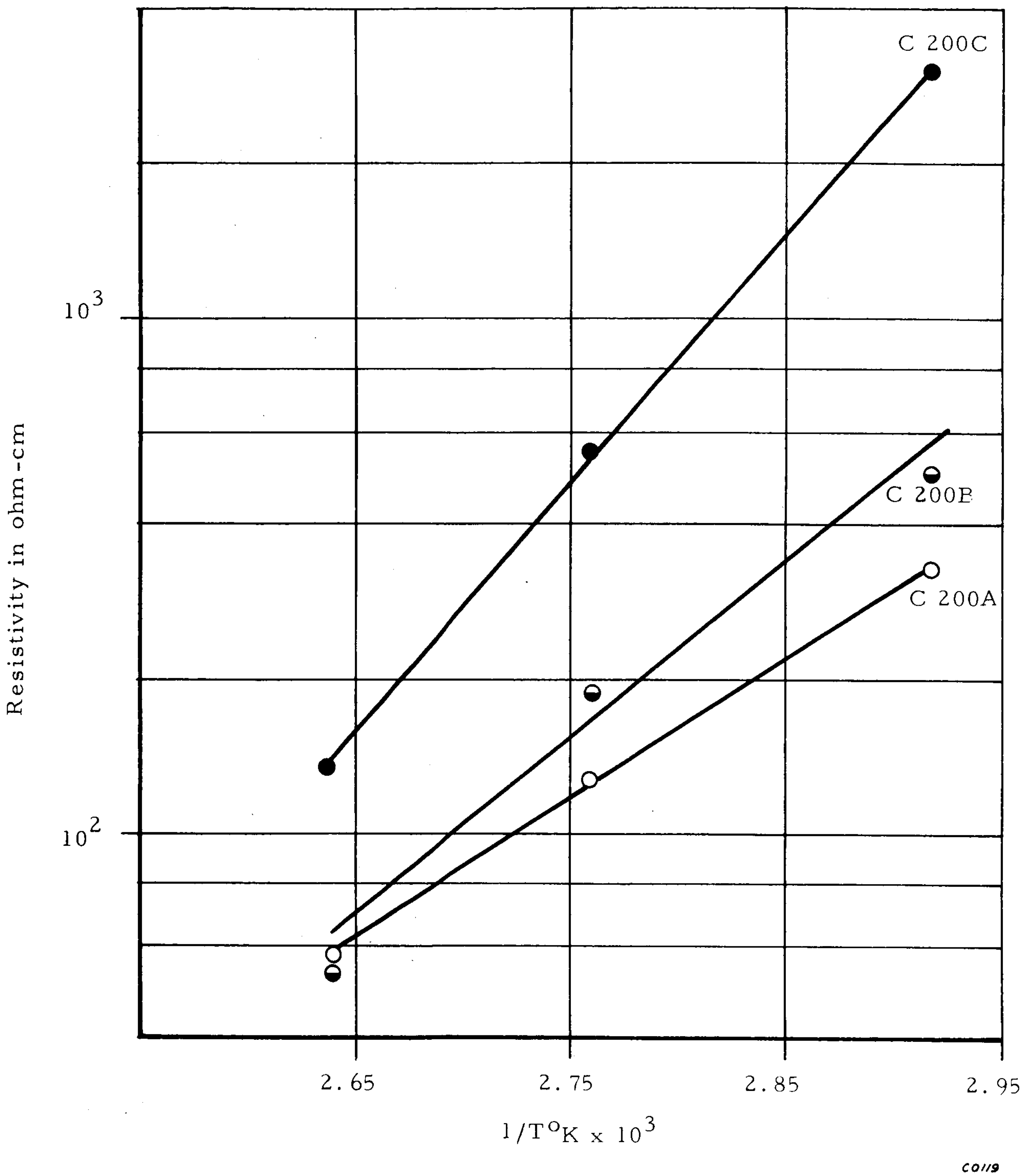


Figure 23. Arrhenius Plot of Log Resistivity vs $1/T\,^{o}K$ for the C200 Membranes at 90% Relative Humidity

TABLE V

SUMMARY OF CONDUCTIVITY ACTIVATION ENERGIES in k cal/mol OVER THE 70°- 90°C RANGE FOR THE C 200 MEMBRANES

50% Relative Humidity

C200A	3.3	C400A	8.6	C600A	4.2	C800A	0.6
C200B	3.4	C400B	5.0	C600B	3.8	C800B	1.7
C200C	3.8	C400C	4.8	C600C	5.3	C800C	3.1

70% Relative Humidity

C200A	7.9	C400A	7.8	C600A	8.6	C800A	4.5
C200B	7.7	C400B	8.3	C600B	8.6	C800B	4.5
C200C	11.8	C400C	6.2	C600C	5.6	C800C	8.6

90% Relative Humidity

C200A	11.2	C400A	13.9	C600A	13.0	C800A	8.5
C200B	16.2	C400B	11.6	C600B	15.2	C800B	7.7
C200C	21.5	C400C	26.0	C600C	7.1	C800C	26.0

solution. Prior blank determinations showed that the correction for carbon dioxide content was negligible under these conditions. Gravimetric determinations with ammoniacal silver nitrate solution afforded yellow precipitates characteristic of the phosphate group, proving that the acid being titrated was phosphoric.

After each one-hour immersion period, the sample was re-immersed under distilled water and the same operation was repeated. Each membrane was oven-dried at 120°C and weighed at the start of the first immersion period so that the weight of phosphoric acid liberated could be computed on a percentage by weight of original dry membrane basis. The results obtained are summarized in Table VI for the determinations based on the total amount of phosphoric acid liberated by the end of the second one-hour immersion period.

It is to be noted from Table VI that the sintering temperature appears to govern stability to hydrolysis mainly, with the composition and presintering temperatures having little or no effect. Membranes sintered at 800°C have the highest stability and there seems to be a tendency for the members containing higher ratios of phosphoric acid to zirconia in the presintered mixture to be the least stable of the systems sintered at 800°C.

A second series of measurements has consisted of analysis for phosphoric acid content derived from exhaustive treatment of the membrane with hot caustic after the membrane had been subjected to a fuel cell determination. In this study the dried membrane was treated with 0.1 N sodium hydroxide at 73° - 75°C for at least two hours. Then the caustic solution was removed by filtration and titrated against 0.1 N hydrochloric acid. This procedure was repeated until the caustic solution no longer manifested any evidence of phosphoric acid. The results obtained for several membranes of the C200B class are summarized in Table VII.

As shown in Column 4 of Table VII, the amount of phosphoric acid recovered from the original membrane is 21.4% based on the dry weight of membrane. The corresponding percentages of phosphoric acid recovered by this treatment following the indicated fuel cell run, based on the dry membrane, are given in Column 5. The difference in values between

TABLE VI

SUMMARY OF DATA ON HYDROLYSIS CONDUCTED AT 73^{o}-75^{o}C ON VARIOUS ZIRCONIUM DIOXIDE-PHOSPHORIC ACID - "ZEOLON H" MEMBRANE SYSTEMS[a,b]

Sample Identification	Sintering Temperature °C 300	500	800
H200	23.8	6.9	0.0
A200	16.7	7.5	0.1
A600	24.7	4.9	2.4
B200	19.4	2.7	0.2
B600	21.5	12.2	2.6
C200	18.9	5.5	1.4
C400	20.3	-	0.7
C600	21.4	14.5	2.4
C800	22.2	13.5	0.5
D200	19.3	15.5	5.0
D600	20.2	13.0	3.9
E200	12.4	8.9	14.9
E600	22.1	16.3	1.2

Increasing ZrO_2 Concentration in pre-sintered Mixture

(a) Expressed as total weight of phosphoric acid extracted divided by original weight of membrane X100.

(b) Values are based on averages of two determinations.

TABLE VII

SUMMARY OF RESULTS OF ANALYSIS FOR PHOSPHORIC ACID FROM MEMBRANE C200B AFTER INDICATED FUEL CELL RUN

Fuel Cell Test No. of Table I	Temp. of Fuel Cell Run, °C	Length of Fuel Cell Run, hrs.	% H_3PO_4 Recovered Originally[a]	% H_3PO_4 Recovered After Fuel Cell Run[a]	% H_3PO_4 Lost During Fuel Cell Run[a]
1	25	624	21.4	19.6	1.8
4	64	288	21.4	21.4	0
5	64	1,174	21.4	7.6	13.8
10	75	52	21.4	20.0	2.8

(a) Based on dry membrane weight

Columns 5 and 6 represents the loss in free phosphoric acid during the indicated fuel cell run. Now from stoichiometric considerations, it is calculated that the total percentage of phosphoric acid derived from the membrane should be 50.6%. This means that 29.2% of the phosphate content of the membrane cannot be recovered from the membrane by the hot caustic hydrolysis treatment it could be tied up as ZrP_2O_7. Therefore, it appears that the phosphoric acid obtained from the treatment with hot water (Table VI) and hot caustic (Table VII) as well as that which is lost during fuel cell operation is unreacted, free phosphoric acid and not that derived from the hydrolysis of zirconium phosphate. Such unreacted phosphoric acid if anything, may serve to strengthen the membrane by hydrogen bonding.

Currently, a fuel cell test is in progress at 67°C where a C200B is being used which had been immersed previously in water at 75°C for two hours to remove free H_3PO_4. Based on the data of Table VI it is estimated that this membrane had lost 5.5% by weight of its free H_3PO_4 content by the prior treatment. After over 168 hours of operation to date at 30 ma/cm^2, the cell voltage is above 0.65v, which compares favorably with any of the data of Table I. According to Column 6 of Table VII, only in the case of fuel cell Test 5 was the loss in free phosphoric acid higher than 5.5%. Since at least that much loss in phosphoric acid when the C200B membrane is involved is not deleterious to fuel cell performance, then the losses indicated for Tests 1 and 10 were not catastrophic. The fact that Test 5 was still capable of performing after the membrane had lost 13.8% its weight in phosphoric acid by the end of 1,174 hours of operation, is additional evidence for the non-critical nature of the free phosphoric acid involved.

4.0 ADDITIONAL STUDIES

A meeting was held at Astropower Laboratory on November 19 and 20, 1964 with the following NASA-Lewis representatives; Dr. B. Lubarsky, Mr. H. Schwartz and Mr. D. Soltis. The project progress to date was reviewed and the future direction of the program was established. It was recognized that the presently employed inorganic membranes were satisfactory for present fuel cell tests. However, it was decided, in the interests of furthering the fuel cell study, that efforts toward membrane improvement would be limited. Instead, major efforts will be directed to the design of an improved fuel cell incorporating a superior electrode - catalyst system, with improved catalyst-membrane contact as well as a system possessing sound water management technique. More truly representative results could be attained thereby for the membrane presently being used. Current progress in this new direction is given below.

The following laboratory efforts were initiated and will be continued during the next quarter.

a) Catalyst: Electrodeposition of platinum on to the membrane matrix is being attempted. The results will be compared with those obtained by the sintering process mentioned above. The vapor deposition of platinum black will be attemped as well. This work will be performed in equipment available at Astropower. Platinum-iridium alloys, palladium-silver alloys and nickel boride will be substituted for platinum in fuel cell tests as part of this program.

b) Electrode: American Cyanamid has agreed to furnish this program with their research tantalum-teflon electrodes having higher platinum content. In addition, they will furnish us with their polyacrylonitrile acid-resistant paper electrodes for our comparative evaluation. Silk, stainless steel and tantalum wire meshes are being evaluated as electrode matrices with silicones as possible replacement for teflon as hydrophobic material.

c) Fuel Cell Design: Mass transfer calculations on the removal of water by evaporation from a wet surface by both a stagnant and a turbulent gas stream favor the use of the latter to prevent electrode and backup plate flooding. This feature will be incorporated in the improved fuel cell design.

5.0 PROJECT PERSONNEL

The following Astropower staff members are connected with the program at this time; Dr. C. Berger, Principal Investigator, Dr. M. P. Strier, Dr. L. O. Rutz, Mr. F. C. Arrance, Mr. G. Belfort and Mr. A. G. Rosa.

6.0 REFERENCES

1. "Investigation of Zeolite Membrane Electrolytes for Fuel Cells" NASA Contract NAS 7-150, Final Report Astropower, Inc., Report 108F, March 1964

2. "Inorganic Ion Exchange Membrane Fuel Cell," NASA-Lewis Research Center Contract NAS 3-6000, Quarterly Progress Report SM-46221-Q1, Period Ending October 10, 1964

3. "Inorganic Ion Exchange Membrane Fuel Cell" NASA-Lewis Research Center Contract NAS 3-6000, Monthly Progress Report for Period Ending 10 November 1964

4. "Inorganic Ion Exchange Membrane Fuel Cell" NASA-Lewis Research Center Contract NAS 3-6000, Monthly Progress Report for Period Ending 10 December 1964